Protonation and Deprotonation Reactions of Triruthenium Nona- and Octa-carbonyl Clusters containing a μ_3-2-Amido-6-methylpyridine (μ_3-ampy) Ligand. *X*-Ray Structures of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ and of One of the Two Isolated Isomers of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$[†]

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The complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) reacts with $HBF_4{\cdot}OEt_2$ to give the dihydride $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**), the structure of which has been determined by *X*-ray diffraction [monoclinic, space group *C*2/*c*, *a* = 23.468(6), *b* = 15.524(6), *c* = 15.283(3), β = 122.83(2)°, *Z* = 8]. Compound (**2**) reacts with NEt_3 regenerating (**1**) and with potassium methoxide giving a mixture of (**1**) and two isomers [(**3**) and (**4**)] of the methoxycarbonyl complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_8]$. Complexes (**1**) and (**2**) react with PPh_3 to give $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_8(PPh_3)]$ (**5**) and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$ (**6**), respectively. In both cases substitution has taken place selectively at an equatorial position *cis* to the NH fragment and *cis* to one hydride and, in the case of complex (**2**), on the Ru atom bonded to only one hydride ligand. Complex (**5**) undergoes protonation with $HBF_4{\cdot}OEt_2$ to give $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$ (**7**). The *X*-ray structure of (**7**)$\cdot OEt_2$ [triclinic, space group $P\bar{1}$, *a* = 10.657(5), *b* = 12.318(3), *c* = 16.622(3) Å, α = 99.14(2), β = 104.18(1), γ = 92.76(1)°, *Z* = 2] shows that the PPh_3 ligand is now on the Ru atom bonded to the two hydrides and *trans* to the hydride which spans the edge bridged by the amido group. Compounds (**6**) and (**7**) are isomers; the former can be converted into the latter upon heating in refluxing tetrahydrofuran. Treatment of complex (**7**) with NEt_3 or potassium methoxide results in deprotonation giving (**5**). However, although the reaction of (**6**) with NEt_3 also gives (**5**), the reaction of (**6**) with potassium methoxide leads to the methoxycarbonyl complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_7(PPh_3)]$ (**8**). Arguments are presented which suggest that in the reactions leading to (**3**), (**4**), and (**8**), the attack of the methoxide ion takes place at equatorial CO ligands bonded to the ruthenium atoms which are attached to two hydrides. Proton and $^{31}P\text{-}\{^1H\}$ n.m.r. and i.r. spectra of all the compounds are also included and discussed in relation to their structures.

Deprotonation reactions of hydridotriruthenium carbonyl clusters have been very little studied[1–4] and although quite a few reports describing protonation of triruthenium carbonyl clusters have appeared,[2–9] as far as we are aware, systematic studies, which would indicate why the reactions take place at specific sites of the clusters, have not been reported. The effect of protonation prior to carbonyl substitution in triruthenium clusters has not been studied either.

In view of these facts, we decided to investigate carbonyl substitution followed by protonation, protonation followed by carbonyl substitution, and also some deprotonation reactions, with the complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (**1**) (Hampy = 2-amino-6-methylpyridine) as the starting material. We chose this complex because it is easy to work with (is thermal- and air-stable), it can be prepared in high yield,[10] and it contains a methyl on the pyridine ring which permits the monitoring of the reactions by ^1H n.m.r. spectroscopy very easily. Furthermore, the presence of the triply bridging ampy ligand enhances the basic character of the Ru–Ru bonds, facilitates the substitution of CO ligands owing to its *cis*-labilizing effect, and prevents cluster degradation. A small part of this work has been communicated in a preliminary form.[11]

Results and Discussion

The complex $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_9]$ (**1**) was recovered unchanged after treatment with triethylamine or potassium methoxide, indicating a very low acidity of the hydride and the NH hydrogen atoms. However, it was easily protonated with $HBF_4{\cdot}OEt_2$ to give the cationic dihydride $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9][BF_4]$ (**2**) (Scheme). The identity of complex (**2**) was suggested by its i.r. spectrum, which showed the ν(CO) absorptions shifted to higher wavenumbers than those of complex (**1**)[10] (as expected for a higher formal oxidation state of the metal atoms) and by its ^1H n.m.r. spectrum (Table 1), which showed two inequivalent hydrides. This was confirmed by an

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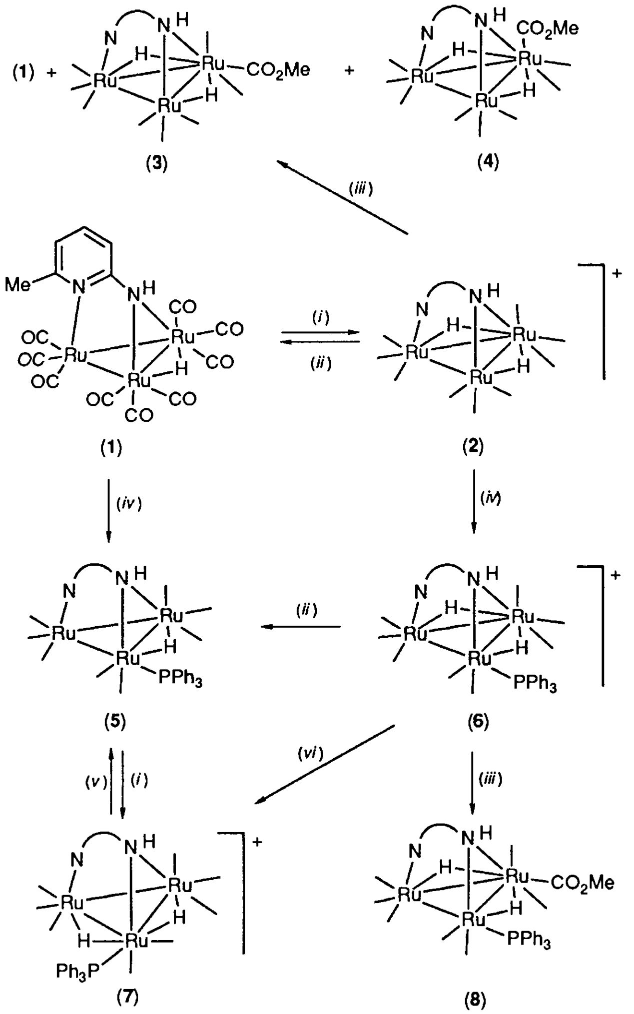
[†] Nonocarbonyl-$1\kappa^3C,2\kappa^3C,3\kappa^3C$-di-μ-hydrido-$1{:}2\kappa^2$; $1{:}3\kappa^2$-μ_3-6-methyl-2-pyridyl-$3\kappa N$-amido-$1{:}2\kappa^2N$-*triangulo*-triruthenium tetrafluoroborate and octacarbonyl-$1\kappa^2C,2\kappa^3C,3\kappa^3C$-di-μ-hydrido-$1{:}2\kappa^2$; $1{:}3\kappa^2$-μ_3-6-methyl-2-pyridyl-3κN-amido-$1{:}2\kappa^2N$–triphenylphosphine-$1\kappa P$-*triangulo*-triruthenium tetrafluoroborate–diethyl ether (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme. (*i*) H^+; (*ii*) NEt_3; (*iii*) MeO^-; (*iv*) PPh_3; (*v*) NEt_3 or MeO^-; (*vi*) heat

X-ray structure determination (Figure 1), which is discussed below.

Treatment of complex (**2**) with triethylamine resulted in deprotonation, giving the neutral complex (**1**). However, reaction with potassium methoxide led to a mixture of three neutral complexes, in a ratio of 1:4:1.2, the minor component being complex (**1**). The ^1H n.m.r. spectrum of the mixture indicated that the two major components were dihydride complexes, showing, as well as the resonances of the ampy ligands, two singlets at δ 3.52 and 3.71 (integral ratio 4:1.2) assignable to methoxycarbonyl groups.[12] The presence of these ligands was also suggested by the i.r. spectrum, which contained a strong band at 1 605 cm^{-1}, absent in the spectrum of complex (**1**). It is reasonable to think that the two equatorial CO groups which are on the H–Ru–H moiety of complex (**2**) (both are *cis*

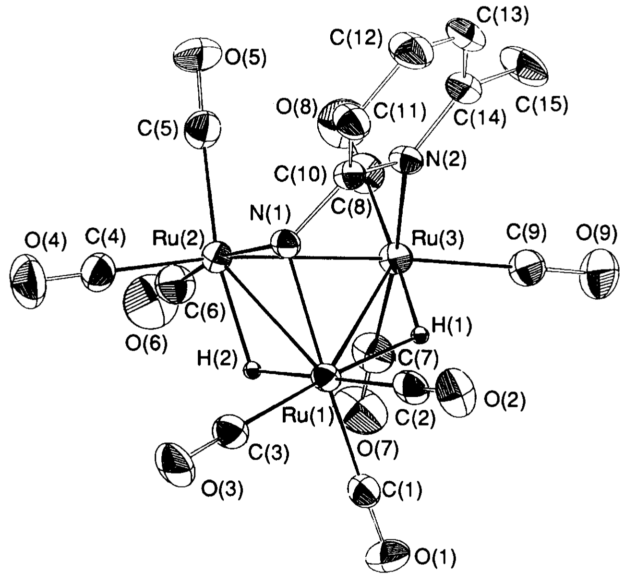
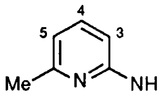


Figure 1. ORTEP diagram of the cation $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_9]^+$ (**2**) showing the atomic numbering scheme

Table 1. N.m.r. data[a]



Complex	δ(^{1}H)							δ(^{31}P-{^{1}H})/ p.p.m.
	H^3	H^4	H^5	NH	Me	μ-H	Other	
(**2**)	7.38 (d)[b]	7.53 (t)[b]	6.94 (d)[b]	7.18 (s)	2.68 (s)	−13.37 (d, 3.2), −14.74 (d, 3.2)		
(**3**)[c]	6.74 (d)	7.34 (t)	6.65 (d)	5.15 (s)	2.65 (s)	−12.15 (s), −13.59 (s)	3.52 (s, CO_2Me)	
(**4**)[c]	6.88 (d)	7.48 (t)	6.37 (d)	5.10 (s)	2.74 (s)	−12.23 (s), −13.70 (s)	3.71 (s, CO_2Me)	
(**5**)	6.55 (d)	7.13 (t)	5.50 (d)	3.75 (s)	2.64 (s)	−11.10 (d, 9.2)	7.8—7.2 (m, PPh_3)	35.6 (s)
(**6**)[d]			6.33 (d)	7.06 (s)	2.00 (s)	−13.14 (t, 2.8) −14.14 (dd, 18.3, 2.8)	7.6—7.2 (m, PPh_3)	28.8 (s)
(**7**)	6.67 (d)	7.02 (t)	6.53 (d)	6.61 (s)	2.32 (s)	−12.80 (dd, 37.4, 1.3), −13.51 (dd, 13.7, 1.3)	7.6—7.3 (m, PPh_3)	35.5 (s)
(**8**)	6.62 (d)	7.22 (t)	6.21 (d)	5.21 (s)	2.17 (s)	−12.09 (d, 3.8), −13.40 (d, 23.5)	7.4—7.3 (m, PPh_3), 3.62 (s, CO_2Me)	31.5 (s)

[a] Spectra recorded in $CDCl_3$, at 300 (^1H) or 121.7 MHz (^{31}P), 25 °C; chemical shifts (δ) relative to $SiMe_4$ (internal, ^1H) or 85% H_3PO_4 (external, ^{31}P); multiplicity and coupling constants, *J*/Hz, in parentheses. [b] Coupling constants for H^3, H^4, and H^5 are *ca.* 7 Hz in all cases. [c] Interchangeable assignments. [d] The resonances of H^3 and H^4 overlap with those of PPh_3.

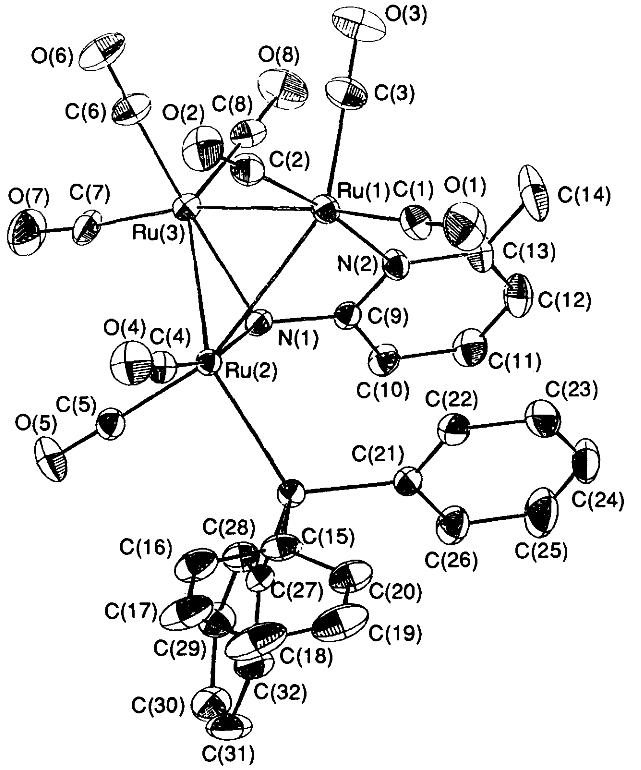


Figure 2. ORTEP diagram of the cation $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_8(PPh_3)]^+$ (**7**) with the atomic numbering scheme

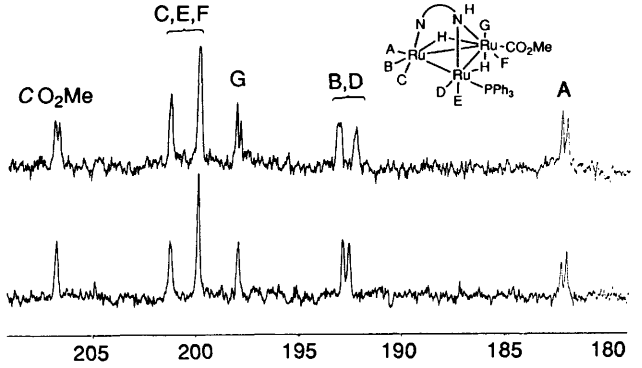


Figure 3. Hydrogen-coupled (above) and hydrogen-decoupled (below) ^{13}C n.m.r. spectra (75.47 MHz, CD_2Cl_2, 25 °C) of a ^{13}CO-enriched sample of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO_2Me)(CO)_7(PPh_3)]$ (**8**)

and *trans* to the two hydrides) bear a higher positive partial charge than the other CO ligands, being therefore more susceptible to nucleophilic attack by the methoxide anion. These arguments induced us to propose for the methoxycarbonyl complexes the structures (**3**) and (**4**) of the Scheme. The formation of methoxycarbonyl groups by attack of methoxide ions on co-ordinated CO ligands is a well established process.[12] The different reactivity observed for triethylamine and methoxide ion is related to their different nucleophilities, the latter being a much stronger nucleophile.

The nonacarbonyl complexes (**1**) and (**2**) reacted with triphenylphosphine at room temperature giving the octacarbonyl derivatives $[Ru_3(\mu\text{-}H)(\mu_3\text{-}ampy)(CO)_8(PPh_3)]$ (**5**) and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_8(PPh_3)][BF_4]$ (**6**), respectively. In both complexes the substituted CO ligands were those *cis* to the amido group and *cis* to one hydride, as inferred from the low *J*(P–H) coupling constant (Table 1) and also because the amido group is a greater *cis* labilizer than pyridine. The ^1H n.m.r. spectrum of complex (**6**) also indicated that the PPh_3 ligand is not attached to the ruthenium atom bonded to the two hydrides, since one of its two P–H couplings constants is very small (2.8 Hz).

Protonation of complex (**5**) with $HBF_4{\cdot}OEt_2$ led to the cationic dihydride $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO)_8(PPh_3)][BF_4]$ (**7**). The protonated edge of (**5**) was that containing the ruthenium atom bonded to triphenylphosphine, since the ^1H n.m.r. spectrum of complex (**7**) showed one hydride *cis* [*J*(P–H) = 13.7 Hz] and the other one *trans* [*J*(P–H) = 37.4 Hz] to the PPh_3 ligand. This result is not surprising because protonation is expected to take place at the most basic Ru–Ru edge and that has to be the edge containing the Ru–PPh_3 moiety. This was confirmed by an *X*-ray structure determination (Figure 2), which is discussed below. However, and surprisingly, the *X*-ray structure also revealed that the PPh_3 ligand had moved from *cis* [in complex (**5**)] to *trans* [in complex (**7**)] to the hydride which spans the amido-bridged Ru–Ru edge. We have found no precedents for such a change of co-ordination site.

Complexes (**6**) and (**7**) are isomers, the latter being thermodynamically more stable, since (**6**) could be converted into (**7**) upon heating in refluxing tetrahydrofuran (thf). Again, the higher basicity of the Ru–Ru–PPh_3 edge is expected to be the driving force for this isomerization.

The reactions of complex (**7**) with triethylamine or potassium methoxide produced deprotonation, leading to complex (**5**). However, although complex (**6**) also underwent deprotonation with triethylamine rendering (**5**), it gave the methoxycarbonyl complex $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO_2Me)(CO)_7(PPh_3)]$ (**8**) on treatment with potassium methoxide. In this case only one isomer was formed. Most probably, the equatorial CO ligand attached to the H–Ru–H moiety of complex (**7**) is not electrophilic enough to react with potassium methoxide due to the presence of the basic PPh_3 ligand on the same metal atom.

It was not possible to obtain crystals of complex (**8**) suitable for *X*-ray diffraction and that prevented the exact location of the methoxycarbonyl group on the cluster. Nevertheless, its presence was shown by i.r. [$\nu(CO_2)$ 1 622 cm^{-1}] and ^1H n.m.r. (Table 1) spectroscopies. The arguments discussed before also suggest that it ought to be in one of the two equatorial positions of the H–Ru–H moiety. This was confirmed by the ^{13}C n.m.r. spectrum of a sample made with ^{13}CO-enriched $[Ru_3(CO)_{12}]$ (Figure 3). The proton-decoupled spectrum only shows one doublet (at δ 182.2 p.p.m., *J* = 19.7 Hz). Since this resonance remains unaltered in the proton-coupled spectrum, we have assigned it to carbonyl A (see assignments in the Figure), which appears to be the only one appreciably coupled to phosphorus. The resonances of the three axial CO ligands (C, E, and F) are also unaltered in the proton-coupled spectrum (the peak at 199.9 p.p.m. contains two coincident resonances), because the *cis* carbonyl–hydride coupling in trinuclear clusters is negligible.[13,14] The remaining four resonances are split into doublets in the proton-coupled spectrum (those at 192.6 and 192.9 p.p.m. split into two overlapping doublets) due to coupling to *trans* hydride ligands. The assignments shown in Figure 3 are based on many other ^{13}C n.m.r. spectra of trinuclear carbonyl complexes containing the ampy ligand.[14] It is also known that for most trinuclear carbonyl clusters the ^{13}C n.m.r. resonances of the equatorial carbonyls occur at lower frequencies than those of the axial ones (attached to the same metal atom).[15] With these data it was impossible to assign unequivocally the position of the methoxycarbonyl ligand of complex (**8**), and therefore the structures depicted in the Scheme and in Figure 3 for this complex correspond to only one of the two possible isomers, the other one being that having the

Table 2. Selected bond distances (Å) and angles (°) in complex (**2**)

Ru(1)–Ru(2)	2.785 5(5)	Ru(2)–Ru(3)	2.743 7(5)
Ru(1)–Ru(3)	2.942 6(5)	Ru(2)–N(1)	2.098(4)
Ru(1)–N(1)	2.106(3)	Ru(2)–C(4)	1.960(6)
Ru(1)–C(1)	1.925(5)	Ru(2)–C(5)	1.914(6)
Ru(1)–C(2)	1.932(6)	Ru(2)–C(6)	1.883(6)
Ru(1)–C(3)	1.946(5)	Ru(2)–H(2)	1.80(6)
Ru(1)–H(1)	1.70(6)	Ru(3)–C(8)	1.876(6)
Ru(1)–H(2)	1.75(6)	Ru(3)–C(9)	1.969(5)
Ru(3)–N(2)	2.177(4)	Ru(3)–H(1)	1.74(6)
Ru(3)–C(7)	1.887(6)		
Ru(3)–Ru(1)–Ru(2)	57.16(1)	Ru(3)–Ru(2)–Ru(1)	64.30(1)
N(1)–Ru(1)–Ru(2)	48.4(1)	N(1)–Ru(2)–Ru(1)	48.64(9)
N(1)–Ru(1)–Ru(3)	70.91(9)	N(1)–Ru(2)–Ru(3)	75.47(9)
C(1)–Ru(1)–Ru(2)	121.4(1)	C(4)–Ru(2)–Ru(1)	103.7(2)
C(1)–Ru(1)–Ru(3)	98.1(1)	C(4)–Ru(2)–Ru(3)	167.9(2)
C(1)–Ru(1)–N(1)	167.8(2)	C(4)–Ru(2)–N(1)	95.4(2)
C(2)–Ru(1)–Ru(2)	143.7(1)	C(5)–Ru(2)–Ru(1)	139.8(2)
C(2)–Ru(1)–Ru(3)	111.5(1)	C(5)–Ru(2)–Ru(3)	93.5(2)
C(2)–Ru(1)–N(1)	95.8(2)	C(5)–Ru(2)–N(1)	95.0(2)
C(2)–Ru(1)–C(1)	93.3(2)	C(5)–Ru(2)–C(4)	95.2(2)
C(3)–Ru(1)–Ru(2)	96.1(2)	C(6)–Ru(2)–Ru(1)	120.9(2)
C(3)–Ru(1)–Ru(3)	153.0(2)	C(6)–Ru(2)–Ru(3)	94.9(2)
C(3)–Ru(1)–N(1)	94.8(2)	C(6)–Ru(2)–N(1)	168.0(2)
C(3)–Ru(1)–C(1)	93.0(2)	C(6)–Ru(2)–C(4)	93.1(3)
C(3)–Ru(1)–C(2)	92.2(2)	C(6)–Ru(2)–C(5)	92.6(2)
H(1)–Ru(1)–Ru(2)	88.4(20)	H(2)–Ru(2)–Ru(1)	37.6(19)
H(1)–Ru(1)–Ru(3)	31.6(20)	H(2)–Ru(2)–Ru(3)	76.3(19)
H(1)–Ru(1)–N(1)	87.4(19)	H(2)–Ru(2)–N(1)	85.4(19)
H(1)–Ru(1)–C(1)	85.5(19)	H(2)–Ru(2)–C(4)	95.2(19)
H(1)–Ru(1)–C(2)	83.5(20)	H(2)–Ru(2)–C(5)	169.4(19)
H(1)–Ru(1)–C(3)	175.3(20)	H(2)–Ru(2)–C(6)	85.4(19)
H(2)–Ru(1)–Ru(2)	39.0(19)	Ru(2)–Ru(3)–Ru(1)	58.54(1)
H(2)–Ru(1)–Ru(3)	71.5(19)	N(2)–Ru(3)–Ru(1)	84.28(9)
H(2)–Ru(1)–N(1)	86.6(19)	N(2)–Ru(3)–Ru(2)	82.8(1)
H(2)–Ru(1)–C(1)	84.8(19)	C(7)–Ru(3)–Ru(1)	87.2(2)
H(2)–Ru(1)–C(2)	176.7(19)	C(7)–Ru(3)–Ru(2)	89.7(2)
H(2)–Ru(1)–C(3)	85.3(19)	C(7)–Ru(3)–N(2)	170.8(2)
H(2)–Ru(1)–H(1)	99.0(27)	C(8)–Ru(3)–Ru(1)	144.8(2)
H(1)–Ru(3)–Ru(1)	30.7(19)	C(8)–Ru(3)–Ru(2)	86.3(2)
H(1)–Ru(3)–Ru(2)	88.9(19)	C(8)–Ru(3)–N(2)	94.5(2)
H(1)–Ru(3)–N(2)	82.6(19)	C(8)–Ru(3)–C(7)	90.3(3)
H(1)–Ru(3)–C(7)	91.9(19)	C(9)–Ru(3)–Ru(1)	115.2(2)
H(1)–Ru(3)–C(8)	174.8(19)	C(9)–Ru(3)–Ru(2)	173.6(2)
H(1)–Ru(3)–C(9)	84.7(19)	C(9)–Ru(3)–N(2)	95.8(2)
Ru(3)–H(1)–Ru(1)	117.6(33)	C(9)–Ru(3)–C(7)	91.2(2)
Ru(2)–H(2)–Ru(1)	103.4(30)	C(9)–Ru(3)–C(8)	100.0(2)
Ru(2)–N(1)–Ru(1)	83.0(1)		

methoxycarbonyl group in the other position on the same ruthenium atom.

X-Ray Structures of Complexes (**2**) *and* (**7**)$\cdot$OEt$_2$.—The structure of compound (**2**) consists of trinuclear cations and BF_4 anions. The cation, with the atomic numbering scheme, is depicted in Figure 1; selected bond distances and angles are given in Table 2. The cluster can be described as a triangle of Ru atoms [Ru(1)–Ru(2) 2.785 5(2), Ru(1)–Ru(3) 2.942 6(5), and Ru(2)–Ru(3) 2.743 7(5) Å] bonded to nine CO groups (three to each metal atom) and to the two nitrogen atoms of an ampy ligand. The Ru(1)–Ru(2) and Ru(1)–Ru(3) edges are bridged by hydrides [Ru(1)–H(1) 1.70(6), Ru(3)–H(1) 1.74(6), Ru(1)–H(2) 1.75(6), and Ru(2)–H(2) 1.80(6) Å], with the Ru(1)–H(2)–Ru(2) and Ru(1)–H(1)–Ru(3) planes forming dihedral angles with the metal triangle of 79(2) and 10(2)°, respectively. The ampy ligand is bonded to the Ru(3) through the pyridinic nitrogen N(2) [Ru(3)–N(2) 2.177(4) Å], while the exocyclic nitrogen N(1) bridges the other two Ru atoms [Ru(1)–N(1) 2.106(3) and Ru(2)–N(1) 2.098(4) Å], the planes Ru(1)–N(1)–Ru(2) and that of the pyridine ring being almost perpendicular to the Ru_3 plane [dihedral angles 93.0(4) and 90.9(5)°, respectively]. The three axial CO ligands are approximately *trans* to the N–Ru bonds, while two of the six equatorial CO ligands are *trans* to the Ru(2)–Ru(3) bond and the remaining four are *trans* to the hydride atoms. This structure is reminiscent of that of [Ru_3(μ-H)(μ_3-anpy)(CO)$_9$] (Hanpy = 2-anilinopyridine),[10] in which one of the two hydride-unbridged Ru–Ru edges has been protonated, producing a lengthening of the edge (*ca.* 0.2 Å) and the movement of two CO ligands from *trans* to that edge to *trans* to the entering hydride.

The structure of compound (**7**)$\cdot$OEt$_2$ consists of trinuclear cations, BF_4 anions, and diethyl ether molecules of crystallization. A diagram of the cation, with the atomic numbering scheme, is shown in Figure 2; selected bond distances and angles are given in Table 3. The cation is very similar to that of complex (**2**) in which a PPh_3 ligand substitutes the equatorial CO group *trans* to the amido-bridged Ru–Ru edge and *cis* to the other hydride. In this case the dihedral angles formed by the metal triangle with the planes Ru(2)–N(1)–Ru(3) and that of the pyridine ring are 87.5(2) and 89.3(5)°, respectively. The two hydrides could not be located, but their presence is evident from the positions of the PPh_3 and the C(3)O(3), C(5)O(5), and C(8)O(8) carbonyl ligands, which are *trans* to hydrides instead of to Ru–Ru edges, and from the lengths of the Ru–Ru bonds [Ru(1)–Ru(2) 2.989 2(9), Ru(1)–Ru(3) 2.743 6(9), and Ru(2)–Ru(3) 2.804 1(9) Å]. Thus the two hydrides span the Ru(1)–Ru(2) and Ru(2)–Ru(3) edges. Although the BF_4 anion is disordered, a very weak hydrogen bridge between the amido nitrogen and one of the fluorine atoms was observed [N(1) $\cdots$ F(1) 2.98(1), F(1) $\cdots$ H(1) 2.1(1), N(1)–H(1) 0.9(1) Å, N(1)–H(1) $\cdots$ F(1) 168(9)°].

Experimental

Solvents were dried and distilled prior to use. All reactions were carried out under nitrogen, using standard Schlenk techniques. Complex (**1**) was prepared by a literature method;[10] all other reagents were obtained from Aldrich and used as received. Instrumentation was as follows: Perkin-Elmer FT 1720-X (i.r.), Bruker AC-300 (n.m.r.), and Perkin-Elmer 240-B (microanalysis).

Preparation of [Ru_3(μ-H)$_2$(μ_3-ampy)(CO)$_9$][BF_4] (**2**).—An excess of $HBF_4\cdot OEt_2$ (0.1 cm^3) was added to a solution of complex (**1**) (200 mg, 0.301 mmol) in dichloromethane (10 cm^3). The solution changed from orange to yellow. After stirring (30 min), the solvent was removed under reduced pressure, the residue washed with diethyl ether (three 5-cm^3 portions), and crystallized from dichloromethane–diethyl ether to give complex (**2**) as yellow crystals (180 mg, 80%) (Found: C, 24.2; H, 1.1; N, 3.5. $C_{15}H_9BF_4N_2O_9Ru_3$ requires C, 24.0; H, 1.2; N, 3.75%). I.r. (cm^{-1}): ν(CO)(thf) 2 129m, 2 101s, 2 087s, 2 076s, 2 064m, 2 039m, 2 026s, 1 966w; ν(NH)(Nujol) 3 280m.

Reactions of Complex (**2**).—*With triethylamine.* Triethylamine (0.1 cm^3) was added to a solution of complex (**2**) (50 mg, 0.066 mmol) in dichloromethane (5 cm^3). The colour changed immediately from yellow to orange. The i.r. spectrum of the solution showed that it contained only complex (**1**).

With potassium methoxide. A solution of KOH in methanol (0.6 cm^3, 0.1 mol dm^{-3}, 0.06 mmol) was added to a solution of complex (**2**) (40 mg, 0.053 mmol) in thf (5 cm^3). The reaction was instantaneous (i.r. spectroscopy). The solution was evaporated to dryness and the residue extracted with dichloromethane (two 5-cm^3 portions) to remove KBF_4.

Table 3. Selected bond distances (Å) and angles (°) in complex (**7**)·OEt_2

Ru(1)–Ru(2)	2.989 2(9)	Ru(1)–Ru(3)	2.743 6(9)
Ru(2)–Ru(3)	2.804 1(9)	Ru(1)–N(2)	2.202(7)
Ru(1)–C(1)	1.944(9)	Ru(1)–C(2)	1.917(9)
Ru(1)–C(3)	1.90(1)	Ru(2)–N(1)	2.145(6)
Ru(2)–P	2.384(2)	Ru(2)–C(4)	1.901(9)
Ru(2)–C(5)	1.903(8)	Ru(3)–N(1)	2.136(6)
Ru(3)–C(6)	1.90(1)	Ru(3)–C(7)	1.940(9)
Ru(3)–C(8)	1.916(9)	N(1)–C(9)	1.384(9)
N(2)–C(9)	1.35(1)	P–C(15)	1.821(8)
P–C(21)	1.823(8)	P–C(27)	1.832(8)
Ru(3)–Ru(1)–Ru(2)	58.38(2)	N(2)–Ru(1)–Ru(2)	84.0(2)
N(2)–Ru(1)–Ru(3)	82.8(2)	C(1)–Ru(1)–Ru(2)	115.4(3)
C(1)–Ru(1)–Ru(3)	173.7(3)	C(1)–Ru(1)–N(2)	98.1(3)
C(2)–Ru(1)–Ru(2)	88.1(3)	C(2)–Ru(1)–Ru(3)	89.3(3)
C(2)–Ru(1)–N(2)	171.0(3)	C(2)–Ru(1)–C(1)	89.2(4)
C(3)–Ru(1)–Ru(2)	145.1(3)	C(3)–Ru(1)–Ru(3)	86.7(3)
C(3)–Ru(1)–N(2)	92.8(3)	C(3)–Ru(1)–C(1)	99.5(4)
C(3)–Ru(1)–C(2)	91.2(4)	Ru(3)–Ru(2)–Ru(1)	56.43(2)
N(1)–Ru(2)–Ru(1)	70.4(2)	N(1)–Ru(2)–Ru(3)	49.0(2)
P–Ru(2)–Ru(1)	110.71(5)	P–Ru(2)–Ru(3)	146.12(5)
P–Ru(2)–N(1)	98.1(2)	C(4)–Ru(2)–Ru(1)	98.7(3)
C(4)–Ru(2)–Ru(3)	117.7(3)	C(4)–Ru(2)–N(1)	165.8(3)
C(4)–Ru(2)–P	94.3(3)	C(5)–Ru(2)–Ru(1)	155.9(3)
C(5)–Ru(2)–Ru(3)	99.6(3)	C(5)–Ru(2)–N(1)	96.5(3)
C(5)–Ru(2)–P	90.6(3)	C(5)–Ru(2)–C(4)	90.3(4)
Ru(2)–Ru(3)–Ru(1)	65.19(2)	N(1)–Ru(3)–Ru(1)	75.9(2)
N(1)–Ru(3)–Ru(2)	49.2(2)	C(6)–Ru(3)–Ru(1)	93.2(3)
C(6)–Ru(3)–Ru(2)	119.9(3)	C(6)–Ru(3)–N(1)	167.0(3)
C(7)–Ru(3)–Ru(1)	169.7(3)	C(7)–Ru(3)–Ru(2)	104.5(3)
C(7)–Ru(3)–N(1)	96.9(3)	C(7)–Ru(3)–C(6)	92.9(4)
C(8)–Ru(3)–Ru(1)	92.4(3)	C(8)–Ru(3)–Ru(2)	141.0(3)
C(8)–Ru(3)–N(1)	96.0(3)	C(8)–Ru(3)–C(6)	91.4(4)
C(8)–Ru(3)–C(7)	95.8(4)	Ru(3)–N(1)–Ru(2)	81.8(2)
C(9)–N(1)–Ru(2)	122.4(5)	C(9)–N(1)–Ru(3)	117.6(5)
C(9)–N(2)–Ru(1)	114.3(5)	C(13)–N(2)–Ru(1)	126.1(6)
C(13)–N(2)–C(9)	119.6(7)	C(15)–P–Ru(2)	114.8(3)
C(21)–P–Ru(2)	114.4(3)	C(21)–P–C(15)	104.3(4)
C(27)–P–Ru(2)	114.4(3)	C(27)–P–C(15)	102.6(4)
C(27)–P–C(21)	105.0(4)	N(2)–C(9)–N(1)	119.1(7)

Removal of the solvent followed by addition of hexane (3 cm^3) led to a yellow solid. Proton n.m.r. analysis (Table 1) of this material indicated that it was a mixture of the complexes (**1**), (**3**), and (**4**) [or (**1**), (**4**), and (**3**)] in a ratio of 1:4:1.2.

Preparation of $[Ru_3(\mu\text{-}H)(\mu_3\text{-ampy})(CO)_8(PPh_3)]$ (**5**).—A solution of triphenylphosphine (27 mg, 0.103 mmol) and complex (**1**) (66 mg, 0.098 mmol) in thf (5 cm^3) was stirred for 45 min. The solvent was removed under reduced pressure and the residue crystallized from thf–diethyl ether to give the solvate (**5**)·thf as an orange solid (70 mg, 74%) (Found: C, 45.0; H, 3.3; N, 3.1. $C_{36}H_{31}N_2O_9PRu_3$ requires C, 44.6; H, 3.2; N, 2.9%). I.r (cm^{-1}): ν(CO)(CH_2Cl_2) 2 060s, 2 021s, 1 992s, 1 980m, 1 958m, 1 940m; ν(NH)(Nujol) 3 280m.

Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$ (**6**).—Triphenylphosphine (18 mg, 0.069 mmol) was added to a solution of complex (**2**) (50 mg, 0.066 mmol) in thf (5 cm^3). After stirring for 30 min the solution was worked-up as for complex (**5**), giving (**6**) as yellow-orange crystals (55 mg, 85%) (Found: C, 38.8; H, 2.55; N, 2.75. $C_{32}H_{24}BF_4N_2O_8PRu_3$ requires C, 39.05; H, 2.45; N, 2.85%). I.r. (cm^{-1}): ν(CO)(thf) 2 133m, 2 081vs, 2 054m, 2 028m, 2 010m, 1 957w; ν(NH)(Nujol) 3 283m.

Table 4. Fractional atomic co-ordinates for the non-hydrogen atoms of complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	0.169 27(2)	0.782 86(2)	0.252 04(3)
Ru(2)	0.034 77(2)	0.800 25(2)	0.087 27(3)
Ru(3)	0.098 51(2)	0.651 72(2)	0.088 31(3)
N(1)	0.125 5(2)	0.842 3(2)	0.105 3(2)
N(2)	0.128 8(2)	0.731 2(2)	0.002 9(3)
O(1)	0.207 9(2)	0.667 5(3)	0.437 7(3)
O(2)	0.315 2(2)	0.810 6(3)	0.314 3(3)
O(3)	0.172 5(3)	0.946 0(3)	0.366 7(4)
O(4)	−0.008 9(3)	0.977 1(3)	0.123 5(4)
O(5)	−0.045 8(2)	0.813 9(3)	−0.148 3(3)
O(6)	−0.077 4(3)	0.708 4(4)	0.090 1(5)
O(7)	0.060 0(3)	0.568 1(3)	0.227 5(4)
O(8)	−0.036 7(2)	0.598 5(3)	−0.101 4(4)
O(9)	0.179 7(3)	0.488 9(3)	0.106 9(4)
C(1)	0.193 9(2)	0.711 1(3)	0.370 2(4)
C(2)	0.262 2(3)	0.797 0(3)	0.291 9(4)
C(3)	0.172 3(3)	0.887 8(3)	0.324 2(4)
C(4)	0.008 5(3)	0.913 6(4)	0.110 5(4)
C(5)	−0.017 6(3)	0.808 7(3)	−0.061 4(4)
C(6)	−0.035 5(3)	0.743 5(4)	0.089 0(5)
C(7)	0.073 7(3)	0.599 1(3)	0.174 3(5)
C(8)	0.015 1(3)	0.619 9(3)	−0.030 4(4)
C(9)	0.153 7(3)	0.551 1(3)	0.101 4(4)
C(10)	0.141 5(2)	0.814 2(3)	0.033 5(3)
C(11)	0.165 8(3)	0.872 6(3)	−0.008 2(4)
C(12)	0.175 3(4)	0.844 6(4)	−0.084 6(5)
C(13)	0.161 2(3)	0.762 0(4)	−0.116 2(4)
C(14)	0.138 3(3)	0.705 4(3)	−0.073 8(4)
C(15)	0.123 7(4)	0.615 4(4)	−0.112 3(5)
B	0.180 7(4)	0.076 3(4)	0.149 4(6)
F(1)	0.202 3(2)	0.122 4(2)	0.238 8(3)
F(2)	0.126 9(2)	0.025 2(2)	0.127 5(4)
F(3)	0.159 2(3)	0.133 0(3)	0.067 9(3)
F(4)	0.232 4(2)	0.027 4(3)	0.160 6(3)

Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO)_8(PPh_3)][BF_4]$ (**7**).—An excess of HBF_4·OEt_2 (0.05 cm^3) was added to a solution of complex (**5**)·thf (50 mg, 0.052 mmol) in dichloromethane (5 cm^3). After stirring for 30 min the solvent was removed under reduced pressure, the residue washed with diethyl ether (three 5-cm^3 portions), and crystallized from dichloromethane–diethylether to give yellow crystals of the solvate (**7**)·OEt_2 (38 mg, 69%) (Found: C, 40.7; H, 3.3; N, 2.5. $C_{36}H_{34}BF_4N_2O_9PRu_3$ requires C, 40.8; H, 3.25; N, 2.65%). I.r. (cm^{-1}): ν(CO)(thf) 2 100m, 2 067vs, 2 019s, 2 005m, 1 990w; ν(NH)(Nujol) 3 295m.

Isomerization of Complex (**6**) *into* (**7**).—A solution of complex (**6**) (40 mg, 0.041 mmol) in thf (8 cm^3) was stirred at reflux temperature for 3 h. The i.r. spectrum of the solution showed complete conversion of complex (**6**) into (**7**).

Deprotonation of Complex (**6**).—A dichloromethane solution (10 cm^3) of complex (**6**) (40 mg, 0.041 mmol) and triethylamine (0.2 cm^3) was stirred for 4 h. The i.r. spectrum of the solution indicated complete conversion of complex (**6**) into (**5**).

Preparation of $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-ampy})(CO_2Me)(CO)_7(PPh_3)]$ (**8**).—A solution of KOH in methanol (0.6 cm^3, 0.1 mol dm^{-3}, 0.06 mmol) was added to a solution of complex (**6**) (43 mg, 0.044 mmol) in thf (5 cm^3), giving a yellow solid. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (eight 5-cm^3 portions), in which it was only sparingly soluble, to remove KBF_4. The extract was evaporated to dryness to give complex (**8**) as a yellow solid (25 mg, 61%) (Found: C, 42.2; H, 2.75; N, 2.7. $C_{33}H_{27}N_2O_9PRu_3$ requires C, 42.65; H, 2.95; N, 2.95%). I.r. (cm^{-1}): ν(CO)(thf) 2 068s, 2 037vs, 2 010s, 1 992m, 1 976m, 1 943w; ν(NH) (Nujol) 3 271m; ν(CO_2)(Nujol) 1 622s.

Table 5. Fractional atomic co-ordinates for the non-hydrogen atoms of complex (7)·OEt_2

Atom	X/a	Y/b	Z/c
Ru(1)	0.250 58(6)	0.237 43(5)	0.115 04(4)
Ru(2)	0.510 01(6)	0.166 21(5)	0.193 11(4)
Ru(3)	0.477 41(6)	0.345 62(5)	0.107 46(4)
O(1)	0.013 4(7)	0.090 9(7)	0.123 4(5)
O(2)	0.249 6(7)	0.078 3(6)	−0.044 0(4)
O(3)	0.110 3(8)	0.401 5(6)	0.014 4(5)
O(4)	0.480 0(7)	−0.059 1(5)	0.082 9(5)
O(5)	0.803 1(6)	0.164 6(6)	0.230 4(5)
O(6)	0.399 6(9)	0.305 8(7)	−0.082 6(5)
O(7)	0.752 4(7)	0.438 8(8)	0.112 2(5)
O(8)	0.362 4(8)	0.567 1(5)	0.113 1(5)
N(1)	0.504 8(6)	0.338 6(5)	0.238 2(4)
N(2)	0.284 3(6)	0.352 9(5)	0.235 4(4)
P	0.507 4(2)	0.100 5(2)	0.320 1(1)
C(1)	0.101 4(8)	0.148 1(8)	0.124 8(6)
C(2)	0.250 3(8)	0.138 7(8)	0.013 5(6)
C(3)	0.162 7(9)	0.339 8(8)	0.052 3(6)
C(4)	0.492 7(8)	0.022 5(7)	0.127 4(6)
C(5)	0.694 2(8)	0.167 2(7)	0.218 7(6)
C(6)	0.431(1)	0.320 4(7)	−0.012 3(6)
C(7)	0.652 9(9)	0.404 1(8)	0.114 9(6)
C(8)	0.405 1(9)	0.485 2(7)	0.111 9(6)
C(9)	0.410 6(7)	0.378 2(6)	0.276 5(5)
C(10)	0.448 1(9)	0.446 6(7)	0.357 3(6)
C(11)	0.353(1)	0.489 4(8)	0.391 6(7)
C(12)	0.226(1)	0.464 5(8)	0.348 7(7)
C(13)	0.191 2(8)	0.397 5(8)	0.269 9(6)
C(14)	0.052(1)	0.375(1)	0.223(1)
C(15)	0.492 6(9)	−0.049 2(6)	0.310 3(5)
C(16)	0.581(1)	−0.107 2(8)	0.276 7(7)
C(17)	0.577(2)	−0.222(1)	0.274 6(8)
C(18)	0.493(2)	−0.275 1(9)	0.305 2(8)
C(19)	0.402(1)	−0.218 5(9)	0.337 8(8)
C(20)	0.406(1)	−0.105 2(8)	0.340 9(7)
C(21)	0.375 4(8)	0.144 9(7)	0.365 8(6)
C(22)	0.248(1)	0.112(1)	0.320 5(7)
C(23)	0.146(1)	0.146(1)	0.353(1)
C(24)	0.172(1)	0.211(1)	0.432(1)
C(25)	0.296(1)	0.240(1)	0.477 4(9)
C(26)	0.400(1)	0.207 5(8)	0.446 3(7)
C(27)	0.655 6(7)	0.141 8(7)	0.405 4(5)
C(28)	0.715 4(9)	0.247 8(7)	0.419 1(6)
C(29)	0.827 7(9)	0.282 4(8)	0.483 2(6)
C(30)	0.881(1)	0.210(1)	0.533 6(7)
C(31)	0.823(1)	0.103(1)	0.520 6(7)
C(32)	0.710 2(9)	0.068 9(8)	0.457 1(6)
B	0.813(1)	0.525(1)	0.353 0(9)
F(1)	0.784 8(7)	0.420 4(6)	0.302 5(5)
F(2)	0.766 9(9)	0.525 3(7)	0.423 0(6)
F(3)	0.925(2)	0.572(1)	0.349(1)
F(4)	0.943(2)	0.511(1)	0.397(1)
F(5)	0.709(2)	0.565(1)	0.298(1)
F(6)	0.823(3)	0.621(2)	0.332(2)
O(40)	0.050(2)	−0.189(1)	0.140(1)
C(41)	0.165(3)	−0.220(2)	0.124(2)
C(42)	0.190(2)	−0.195(2)	0.050(1)
C(44)	0.012(3)	−0.232(2)	0.210(2)
C(45)	−0.080(3)	−0.163(2)	0.236(2)

Crystal Structure Determination of Complex (**2**).—*Crystal data.* $C_{15}H_9BF_4N_2O_9Ru_3$, $M = 751.3$, monoclinic, space group $C2/c$, $a = 23.468(6)$, $b = 15.524(6)$, $c = 15.283(3)$ Å, $\beta = 122.83(2)°$, $U = 4\,679(2)$ Å^3, $Z = 8$, $D_c = 2.13$ g cm^{-3}, $F(000) = 2\,864$, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 19.54 cm^{-1}, crystal dimensions 0.22 × 0.25 × 0.30 mm.

Data collection and processing. CAD-4 Enraf-Nonius diffractometer. The intensities of 3 515 reflections ($1.5 \leqslant \theta \leqslant 25°$, scan width $1.20 + 0.34 \tan\theta$, ω—2θ mode, Mo-K_α radiation, graphite monochromator) were collected. 2 872 Reflections with $F \geqslant 3\sigma(F)$ were used for refinements. Two standard reflections were measured every 2 h, but no change was observed. An absorption correction was applied by an empirical method based on the ψ scan of one reflection[16] (minimum, maximum transmission factors 1.00, 1.25).

Structure solution and refinement. Direct and Fourier methods; least squares in three blocks (337 parameters) with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were found on difference maps and were given an isotropic overall thermal parameter. Atoms were corrected for anomalous dispersion. A secondary extinction correction was made. The final weighting scheme was $1/\Sigma_{r=1-3}$ ArTr(X) with three coefficients 4.62, −3.22, and 3.40 for a Chebishev series where $X = F_o/F_o(\text{max.})$. A final difference map showed no peak higher than 0.4 e Å^{-3} (minimum −0.4 e Å^{-3}). Final R and R' values were 0.0248 and 0.0269. All calculations were performed with CRYSTALS.[17] An ORTEP diagram of the cation is shown in Figure 1. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 4.

Crystal Structure Determination of Complex (**7**)·OEt_2.—*Crystal data.* $C_{36}H_{34}BF_4N_2O_9PRu_3$, $M = 1\,059.6$, triclinic, space group $P\bar{1}$, $a = 10.657(5)$, $b = 12.318(3)$, $c = 16.622(3)$ Å, $\alpha = 99.14(2)$, $\beta = 104.18(1)$, $\gamma = 92.76(1)°$, $U = 2\,080(3)$ Å^3, $Z = 2$, $D_c = 1.68$ g cm^{-3}, $F(000) = 1\,048$, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 11.6 cm^{-1}, crystal dimensions 0.45 × 0.30 × 0.20 mm.

Data collection and processing. Philips PW 1100 diffractometer. The intensities of 5 912 reflections ($1 \leqslant \theta \leqslant 25°$, scan width $0.9 + 0.34 \tan\theta$, ω—2θ mode, Mo-K_α radiation, graphite monochromator) were collected. 5 253 Reflections with $I \geqslant 3\sigma(I)$ were used for refinements. The intensities of two standard reflections showed no variation during the data collection although dark spots appeared on the crystal surface (the crystal was sealed in a capillary glass tube). An absorption correction was applied using the program DIFABS[18] from CRYSTALS.[17]

Structure solution and refinement. Direct and Fourier methods; least squares in two blocks (531 parameters). A difference map revealed the OEt_2 molecule. The BF_4 anion was disordered which was treated by introducing two different positions F(3) and F(4), F(5) and F(6) for two of the four fluorine atoms, with an occupancy factor of 0.5. All non-hydrogen atoms, except those of BF_4 and OEt_2, were refined anisotropically. All hydrogen atoms, except those of the OEt_2 molecule and the two hydrides, were found on difference maps and their co-ordinates refined with an isotropic overall thermal parameter. Atoms were corrected for anomalous dispersion with CRYSTALS.[17] Unit weights were employed. The last difference map showed no peak higher than 1.6 e Å^{-3} (minimum −1.1 e Å^{-3}). Final R and R' values were 0.0491 and 0.0548. The structure is not very accurate due to the very high thermal agitation of the OEt_2 molecule, the disorder of the BF_4 anion, and the low quality of the crystals. This prevented the location of the two hydrides and the OEt_2 hydrogen atoms. An ORTEP diagram of the cation is shown in Figure 2. Final atomic co-ordinates for the non-hydrogen atoms are collected in Table 5.

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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