Complexes of the Platinum Metals. Part 46.[1] 1,1,1,5,5,5-Hexafluoro-3-azapentane-2,4-diiminato Derivatives of Ruthenium, Osmium and Iridium. Crystal Structure of [Ru{NHC(CF$_3$)NC(CF$_3$)NH}H(CO)(PPh$_3$)$_2$]†

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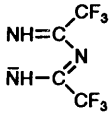
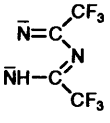
Trifluoroacetamidine, NH=C(CF$_3$)–NH$_2$, underwent a condensation reaction in the presence of certain platinum metal hydrides in boiling toluene to liberate ammonia and form complexes containing the *N,N'*-chelating 1,1,1,5,5,5-hexafluoro-3-azapentane-2,4-diiminate ligand NHC(CF$_3$)NC(CF$_3$)NH. Complexes prepared in this manner were [M{NHC(CF$_3$)NC(CF$_3$)NH}H(CO)(PPh$_3$)$_2$], [M{NHC(CF$_3$)NC(CF$_3$)NH}Cl(CO)(PPh$_3$)$_2$], [M{NHC(CF$_3$)NC(CF$_3$)NH}$_2$(PPh$_3$)$_2$] (M = Ru or Os) and [Ir{NHC(CF$_3$)NC(CF$_3$)NH}H$_2$(PPh$_3$)$_2$]. Under similar conditions [Ru(O$_2$CCF$_3$)$_2$(CO)(PPh$_3$)$_2$] reacted to afford the complex [Ru{NHC(CF$_3$)NC(CF$_3$)NH}(O$_2$CCF$_3$)(CO)(PPh$_3$)$_2$] in which intramolecular hydrogen bonding between the non-co-ordinated oxygen of the monodentate trifluoroacetate ligand and the adjacent NH moiety has been detected. An X-ray crystallographic study performed on [Ru{NHC(CF$_3$)NC(CF$_3$)NH}H(CO)(PPh$_3$)$_2$] has confirmed an octahedral ruthenium(II) structure with *trans*-phosphine ligands and a chelating NHC(CF$_3$)NC(CF$_3$)NH$^-$ moiety.

As part of our ongoing study of platinum metal complexes containing heteroallylic ligands we have recently reported on the synthesis of *N,N'*-diphenylamidinato derivatives from the corresponding amidines PhN=C(R)–NHPh (R = H, Me, Et or Ph).[2] We now describe how attempts to prepare analogous complexes from the *N,N'*-unsubstituted trifluoroacetamidine, NH=C(CF$_3$)–NH$_2$, have yielded products containing the 1,1,1,5,5,5-hexafluoro-3-azapentane-2,4-diiminate ligand NHC(CF$_3$)NC(CF$_3$)NH$^-$ formed by condensation of an amidinate ligand and a molecule of the parent amidine with elimination of a molecule of ammonia. This ligand has previously been encountered only in the complexes [Ir{NHC(CF$_3$)NC(CF$_3$)NH}(CO)(PPh$_3$)$_2$][3] and [Ru{NHC(CF$_3$)NC(CF$_3$)NH}(PPh$_3$)(C$_5$H$_5$)][4] obtained from the reactions of [Ir(C$_3$H$_5$)(CO)(PPh$_3$)$_2$] and [RuCl(PPh$_3$)$_2$(C$_5$H$_5$)] respectively with CF$_3$CN, and in the PPh$_3$–P(OMe)$_3$ exchange product [Ru{NHC(CF$_3$)NC(CF$_3$)NH}{P(OMe)$_3$}(C$_5$H$_5$)].[4] Trifluoromethyl cyanide also reacts with [Pt(PPh$_3$)$_4$] to form the platinum(II) complex [Pt{NC(CF$_3$)NC(CF$_3$)NH}(PPh$_3$)$_2$] containing the closely related dianionic NC(CF$_3$)NC(CF$_3$)NH ligand.[5] The structures displayed have been confirmed by X-ray diffraction studies performed on [Ru{NHC(CF$_3$)NC(CF$_3$)NH}{P(OMe)$_3$}(C$_5$H$_5$)][4] and Pt{NC(CF$_3$)NC(CF$_3$)NH}(PPh$_3$)$_2$][5] respectively. The reactions described in the present paper yield eight new complexes containing the co-ordinated 1,1,1,5,5,5-hexafluoro-3-azapentane-2,4-diiminate anion and offer the first general synthesis of complexes containing this interesting ligand.





Experimental

General experimental conditions were similar to those described in earlier papers in this series.[2] Trifluoroacetamidine and platinum metal salts were obtained from Fluorochem and Johnson Matthey plc respectively. Platinum metal hydrides[6] and the ruthenium trifluoroacetate[7] complex were prepared as previously described. Spectroscopic data are given in Tables 1 and 2.

[Ru{NHC(CF$_3$)NC(CF$_3$)NH}H(CO)(PPh$_3$)$_2$] **1**.—Carbonyldihydridotris(triphenylphosphine)ruthenium (0.8 g, 0.87 mmol) and trifluoroacetamidine (0.4 g, 3.6 mmol) were heated under reflux in toluene (40 cm^3) for *ca.* 40 min. The reddish orange solution was allowed to cool to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation of the oil from dichloromethane–methanol gave the product as yellow plates. Yield 0.46 g (61%), m.p. 224–226 °C (decomp.) (Found: C, 56.9; H, 3.9; N, 4.8. Calc. for C$_{41}$H$_{33}$F$_6$N$_3$OP$_2$Ru: C, 57.2; H, 3.85; N, 4.9%).

[Ru{NHC(CF$_3$)NC(CF$_3$)NH}Cl(CO)(PPh$_3$)$_2$] **2**.—Carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.6 g, 0.65 mmol) and trifluoroacetamidine (0.4 g, 3.6 mmol) were heated together under reflux in toluene (40 cm^3) for *ca.* 4.5 h. The yellow solution was allowed to cool to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation of the oil from dichloromethane–methanol gave the product as yellow

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

microcrystals. Yield 0.45 g (77%), m.p. 246–249 °C (decomp.) (Found: C, 54.55; H, 3.5; N, 4.55. Calc. for $C_{41}H_{32}ClF_6N_3OP_2Ru$: C, 55.0; H, 3.55; N, 4.6%).

$[Ru\{NHC(CF_3)NC(CF_3)NH\}(O_2CCF_3)(CO)(PPh_3)_2]$ **3**.—Carbonylbis(trifluoroacetato)bis(triphenylphosphine)ruthenium (0.5 g, 0.61 mmol) and trifluoroacetamidine (0.3 g, 2.68 mmol) were heated together under reflux in toluene (40 cm^3) for *ca.* 17 h. The yellow solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation of the oil from dichloromethane–methanol gave the product as pale yellow needles. Yield 0.32 g (54%), m.p. 272–276 °C (Found: C, 53.0; H, 3.4; N, 4.15. Calc. for $C_{43}H_{32}F_9N_3O_3P_2Ru$: C, 53.1; H, 3.3; N, 4.3%).

$[Ru\{NHC(CF_3)NC(CF_3)NH\}_2(PPh_3)_2]$ **4**.—*Method A*. Chlorohydridotris(triphenylphosphine)ruthenium (0.8 g, 0.97 mmol) and trifluoroacetamidine (0.5 g, 4.5 mmol) were heated together under reflux in degassed toluene (40 cm^3) for *ca.* 1 h. The reddish orange solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation of the oil from dichloromethane–methanol gave the product as orange plates. Yield 0.58 g (58%), m.p. 260–264 °C (decomp.) (Found: C, 50.7; H, 3.25; N, 7.95. Calc. for $C_{44}H_{34}F_{12}N_6P_2Ru$: C, 50.9; H, 3.25; N, 8.1%).

Method B. The same complex was also obtained from dihydridotetrakis(triphenylphosphine)ruthenium under similar conditions with a reflux time of *ca.* 3 h, and was characterised by spectroscopic comparison with an authentic sample prepared by method A.

$[Os\{NHC(CF_3)NC(CF_3)NH\}H(CO)(PPh_3)_2]$ **5**.—Carbonyldihydridotris(triphenylphosphine)osmium (0.3 g, 0.29 mmol) and trifluoroacetamidine (0.2 g, 1.78 mmol) were heated under reflux in toluene (30 cm^3) for *ca.* 27 h. The yellow solution was cooled to ambient temperature, filtered and concentrated under reduced pressure to leave an oil. Crystallisation of the oil from dichloromethane–methanol gave the product as orange-yellow plates. Yield 0.18 g (67%), m.p. 268–272 °C (Found: C, 51.85; H, 3.7; N, 4.35. Calc. for $C_{41}H_{33}F_6N_3OOsP_2$: C, 51.8; H, 3.45; N, 4.45%).

$[Os\{NHC(CF_3)NC(CF_3)NH\}Cl(CO)(PPh_3)_2]$ **6a**, **6b**.—Carbonylchlorohydridotris(triphenylphosphine)osmium (0.5 g, 0.48 mmol) and trifluoroacetamidine (0.4 g, 3.6 mmol) were heated under reflux in toluene (40 cm^3) for *ca.* 16 h. The yellow solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation of the oil from dichloromethane–methanol gave the product as yellow needles. Yield 0.28 g (60%), m.p. 295–298 °C (decomp.) (Found: C, 49.7; H, 3.35; N, 4.15. Calc. for $C_{41}H_{32}ClF_6N_3OOsP_2$: C, 50.05; H, 3.25; N, 4.25%). Spectroscopic data (Table 1) establish that **6a** is the *cis*-phosphine isomer. Heating a sample of **6a** under reflux in toluene for 47 h followed by work-up as above gave a *ca.* 60:40 mixture of **6a** and the *trans*-phosphine isomer **6b**.

$[Os\{NHC(CF_3)NC(CF_3)NH\}_2(PPh_3)_2]$ **7**.—Tetrahydridotris(triphenylphosphine)osmium (0.6 g, 0.61 mmol) and trifluoroacetamidine (0.5 g, 4.5 mmol) were heated under reflux in toluene (50 cm^3) for *ca.* 6 h. The dark reddish brown solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation of the oil from dichloromethane–methanol gave the product as a dark orange-red solid. A further crystallisation from the same solvent pair gave the pure product as dark orange-red microcrystals. Yield 0.36 g (53%), m.p. 225–230 °C (decomp.) (Found: C, 46.7; H, 3.05; N, 7.15. Calc. for $C_{44}H_{34}F_{12}N_6OsP_2$: C, 46.9; H, 3.0; N, 7.45%).

$[Ir\{NHC(CF_3)NC(CF_3)NH\}H_2(PPh_3)_2]$ **8**.—*mer*-Trihydridotris(triphenylphosphine)iridium (0.3 g, 0.38 mmol) and trifluoroacetamidine (0.3 g, 2.68 mmol) were heated under reflux in toluene (30 cm^3) for *ca.* 3 h. The yellow solution was cooled to ambient temperature, filtered and then concentrated under reduced pressure to leave an oil. Crystallisation of the oil from dichloromethane–methanol gave the product as yellow needles. Yield 0.22 g (63%), m.p. 257–260 °C (Found: C, 51.6; H, 3.5; N, 4.45. Calc. for $C_{40}H_{34}F_6IrN_3P_2$: C, 51.95; H, 3.65; N, 4.55%).

Crystallography.—The crystal used for the X-ray work was a small block of dimensions 0.10 × 0.20 × 0.15 mm mounted with silicone grease on a glass fibre. Cell dimensions and intensity data were recorded at 140 K, as previously described[8] using a FAST TV area detector mounted at the window of a rotating-anode diffractometer operating at 50 kV, 50 mA with a molybdenum anode [λ(Mo-Kα) = 0.710 69 Å]. The crystal-to-detector distance was 50.0 mm and the detector 2θ swing angle was 20°. Slightly more than one hemisphere of data were recorded. Following normal data processing, the structure was solved *via* direct methods[9a] and refined by full-matrix least squares.[9b] A correction for absorption was made using the program DIFABS.[10] Non-hydrogen atoms were refined anisotropically, hydrogen isotropically. Crystal data, details of data collection and refinement are as follows.

Crystal data. $C_{41}H_{33}F_6N_3OP_2Ru$, M 860.71, monoclinic, space group $P2_1/c$, a = 15.590(1), b = 12.084(6), c = 20.943(3) Å, β = 105.99(3)°, U = 3793(2) Å^3, Z = 4, D_c = 1.507 g cm^{-3}, $F(000)$ = 1744, μ(Mo-Kα) = 5.6 cm^{-1}. Intensity data corresponding to the ranges $1.97 < \theta < 25.08°$, $-17 < h < 16$, $-11 < k < 14$, $-20 < l < 23$ were recorded, giving 11 366 data of which 5717 were unique ($I > 2\sigma I$).

Refinement was based on F^2 and involved a total of 443 parameters. Unit weights were used and in the DIFABS process the maximum and minimum correction factors were 1.256 and 1.128. The final R, R' values were 0.0448, 0.1046 [$w = 1/\sigma^2(F_o^2)$] and the maximum excursions in the final difference map were −0.575, +0.48 e Å^{-3}. Final atomic coordinates for non-hydrogen atoms are given in Table 3.

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

Results and Discussion

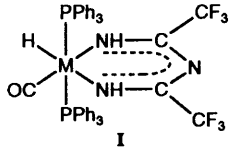
Using reaction conditions similar to those hitherto employed to synthesise *N,N'*-diphenylamidinato complexes from the corresponding *N,N'*-diphenylamidines, PhN=C(R)–NHPh,[2] we have now investigated the reactions of the *N,N'*-unsubstituted amidine NH=C(CF_3)–NH_2 with a range of ruthenium, osmium and iridium hydrides and with one ruthenium trifluoroacetate complex. In each instance a novel amidine condensation reaction occurs leading to the isolation in good yield of products containing the chelate 1,1,1,5,5,5-hexafluoro-3-azapentane-2,4-diiminate ligand. The conditions necessary to drive these reactions to completion are moderately severe (toluene reflux 1–27 h) and with one exception, the isolation of a geometric isomer of the final product from the reaction with $[OsH(Cl)(CO)(PPh_3)_3]$, no intermediate species were detected. In particular no evidence for the formation of intermediates containing monodentate or chelating amidinate ligands was observed although it seems probable that such species do play a part in the formation of the condensed ligand. Reactions performed under milder conditions with a view to detecting such intermediates have to date given only mixtures of starting materials and final products.

$[Ru\{NHC(CF_3)NC(CF_3)NH\}H(CO)(PPh_3)_2]$ **1**.—The reaction of $[RuH_2(CO)(PPh_3)_3]$ with the free amidine in boiling toluene quickly gave the above product in good yield as air-stable yellow crystals. The nitrogen elemental analysis figure

Table 1 Selected ^1H, ^{13}C-{^1H}, ^{19}F and ^{31}P-{^1H} NMR data[a]

			^{13}C-{^1H}							
	^1H, MH		CO		CCF_3		CCF_3			
Complex	δ	$^2J_{HP}$	δ	$^2J_{CP}$	δ	$^2J_{CF}$	δ	$^1J_{CF}$	δ(^{19}F), CF_3	δ(^{31}P-{^1H}), PPh_3
1	−11.37(t)	19.5	204.5(t)	15	154.5(q)	33	117.3(q)	280		
					154.2(q)	33	117.2(q)	280	−75.7	50.6
2	—	—	203.2(t)	14	153.6(q)	33	117.0(q)	280	−75.1	
					153.4(q)	33	116.3(q)	280	−75.5	32.3
3		—	201.8(t)	14	154.0(q)	34	117.2(q)	280		
					152.8(q)	34	116.1(q)	280	−76[b]	
					164.6(q)[c]	36	114.3(q)[c]	290	−76.3[b]	43.0
4	—	—	—	—	154.6(q)	33	117.5(q)	280	−74.1	
					152.4(q)	34	117.2(q)[d]	280	−74.7	46.2
5	−12.16(t)	17	186.0(t)	10	150.7(q)	33	117.3(q)	280	−75.95	
					150.3(q)	33	117.2(q)	280	−76.0	24.8
6a	—	—	182.2(t)	9.5	152.1(q)	34	117.3(q)	280	−74.7	−0.15
6b	—	—	183.6(t)	10	149.5(q)	34	116.8(q)	276	−75.43	
									−75.44	6.0
									−75.66	
7	—	—	—	—	149.1(q)	33	118.1(q)	276	−74.1	
					146.5(q)	33	117.8(q)	276[d]	−74.8	3.0
8	−19.53(t)	17	—	—	149.6(q)	33	117.5(q)	280	−76.3	25.6

[a] All spectra taken in $CDCl_3$ solution, referenced to $SiMe_4$ (^1H and ^{13}C-{^1H}), external $CFCl_3$ (^{19}F) or external 85% H_3PO_4 (^{31}P-{^1H}). Resonances singlets unless otherwise indicated: t = triplet, q = quartet. [b] Broadened signal, see text. [c] Resonance due to $CF_3CO_2^-$ ligand. [d] Resonance shows small additional triplet splittings *J. ca.* 3 Hz.



I

strongly suggested the presence of a $NHC(CF_3)NC(CF_3)NH$ ligand formed by condensation of a molecule of the free amidine with an amidinate ligand. The ^1H NMR spectrum (Table 1) clearly established the presence of a hydride *cis* to a pair of equivalent phosphine ligands. The ^{13}C-{^1H} NMR spectrum displayed four separate resonances, each split into a 1:3:3:1 quartet by coupling to the fluorines of the CF_3 groups, for the four carbon atoms of the postulated $NHC(CF_3)NC(CF_3)NH$ chelate ligand. These data suggest that the condensed ligand is situated in an asymmetric co-ordination environment. The appearance of only a single signal in the ^{19}F NMR spectrum of the complex is therefore attributed to the coincidental overlap of resonances arising from two CF_3 groups in similar but not identical environments. The ^{13}C chemical shifts and the ^{13}C–^{19}F coupling constants $^1J_{CF}$ and $^2J_{CF}$ observed for the 1,1,1,5,5,5-hexafluoro-3-azapentane-2,4-diiminate ligands in this and other complexes described in the present work are in excellent agreement with similar data previously reported for $[Ru\{NHC(CF_3)NC(CF_3)NH\}\{P(OMe)_3\}(C_5H_5)]$.[4] A crystal structure determination (see below) confirmed the predicted structure of the chelate $NHC(CF_3)NC(CF_3)NH$ ligand and the overall stereochemistry **I** (M = Ru) for the complex.

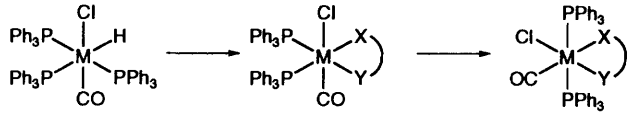
$[Ru\{NHC(CF_3)NC(CF_3)NH\}Cl(CO)(PPh_3)_2]$ **2**.—Reactions of the ruthenium and osmium complexes $[MH(Cl)(CO)(PPh_3)_3]$ with anionic chelating ligands ($x–y^-$) frequently afford kinetically controlled *cis*-phosphine products which subsequently rearrange to the thermodynamically preferred *trans*-phosphine isomers (Scheme 1).

The reaction of $[RuH(Cl)(CO)(PPh_3)_3]$ with the free amidine in boiling toluene over a period of *ca.* 4.5 h gave the product **2** in good yield as air-stable yellow microcrystals. The ^{31}P NMR spectrum contained only a singlet (δ 32.3) and this did not conclusively differentiate between two possible isomeric

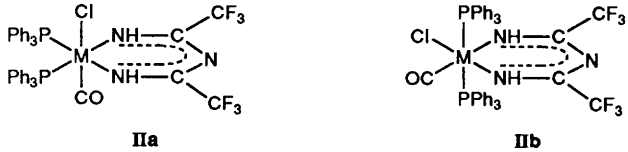
Table 2 Selected infrared data (cm^{-1})*

Complex	ν(MH)	ν(CO)	ν(NH)	ν(C=N)
1	1915	1934	3366	1602, 1553
2	—	1950	3361, 3342	1600, 1550
3	—	1949	3369, 3213(br)	1607, 1541
4	—	—	3348, 3320	1575, 1531
5	2013	1914	3369	1596, 1554
6a	—	1934(br)	3322	1608, 1553
7	—	—	3345, 3312	1573, 1529
8	2140, 2130	—	3367	1604, 1554

* All spectra recorded using Nujol mulls; all absorptions strong and sharp unless otherwise indicated; br = broad.



Scheme 1



IIa **IIb**

products **IIa** and **IIb** (M = Ru). However the ^{13}C-{^1H} and ^{19}F NMR data which reveal the presence of non-equivalent CF_3 groups and hence an asymmetrically located $NHC(CF_3)NC(CF_3)NH$ ligand clearly establish **IIb** as the correct stereochemistry. In contrast to the corresponding osmium system (see below) no evidence for the presence of the kinetic intermediate **IIa** was observed.

$[Ru\{NHC(CF_3)NC(CF_3)NH\}(O_2CCF_3)(CO)(PPh_3)_2]$ **3**.—This product resulted from the reaction of $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$ with free amidine in boiling toluene. Despite the

Table 3 Fractional atomic coordinates ($\times 10^4$) for $[Ru\{NHC(CF_3)NC(CF_3)NH\}H(CO)(PPh_3)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	2483(1)	776(1)	1580(1)	C(24)	−681(3)	−2205(6)	486(4)
F(1)	−628(3)	1265(7)	1258(3)	C(25)	−341(4)	−1921(6)	1152(3)
F(2)	−649(3)	195(6)	2045(3)	C(26)	545(4)	−1597(5)	1393(2)
F(3)	−427(4)	1927(7)	2224(4)	C(31)	2719(3)	−2068(4)	1980(2)
F(4)	3122(4)	140(6)	3908(3)	C(32)	3591(3)	−1892(4)	2361(3)
F(5)	1994(5)	1049(8)	3982(3)	C(33)	3992(3)	−2632(5)	2862(2)
F(6)	1882(4)	−639(7)	3778(3)	C(34)	3522(4)	−3548(4)	2983(2)
P(1)	2252(1)	−1111(2)	1294(1)	C(35)	2649(4)	−3725(4)	2603(3)
P(2)	2739(1)	2686(2)	1794(1)	C(36)	2248(3)	−2985(4)	2101(3)
N(1)	1130(5)	938(6)	1547(4)	C(41)	3563(3)	3359(4)	1446(3)
N(2)	2629(5)	459(5)	2600(3)	C(42)	3681(4)	2983(4)	849(3)
N(3)	1128(5)	707(7)	2664(3)	C(43)	4254(4)	3541(5)	556(2)
O	4386(5)	512(6)	1556(4)	C(44)	4709(3)	4474(5)	860(3)
C(1)	3646(6)	622(7)	1585(5)	C(45)	4591(4)	4850(4)	1457(3)
C(5)	763(5)	884(7)	2031(4)	C(46)	4018(4)	4292(4)	1750(2)
C(2)	2012(5)	478(7)	2909(4)	C(51)	3197(4)	2959(5)	2681(2)
C(3)	−250(6)	1080(10)	1887(5)	C(52)	2708(3)	3426(5)	3076(3)
C(4)	2241(6)	277(10)	3643(5)	C(53)	3108(5)	3607(5)	3748(3)
C(11)	2769(4)	−1640(4)	668(3)	C(54)	3996(5)	3321(6)	4025(2)
C(12)	2919(4)	−2767(4)	622(3)	C(55)	4485(4)	2853(6)	3630(3)
C(13)	3265(5)	−3166(4)	122(3)	C(56)	4086(4)	2673(5)	2958(3)
C(14)	3462(5)	−2438(6)	−332(3)	C(61)	1783(3)	3616(4)	1493(3)
C(15)	3312(5)	−1311(5)	−286(3)	C(62)	1062(4)	3553(5)	1761(3)
C(16)	2966(5)	−911(4)	214(3)	C(63)	326(3)	4235(6)	1521(3)
C(21)	1091(3)	−1558(5)	968(3)	C(64)	310(4)	4980(5)	1012(4)
C(22)	751(4)	−1841(5)	303(3)	C(65)	1031(5)	5043(4)	744(3)
C(23)	−135(4)	−2165(5)	62(2)	C(66)	1767(4)	4361(5)	984(3)

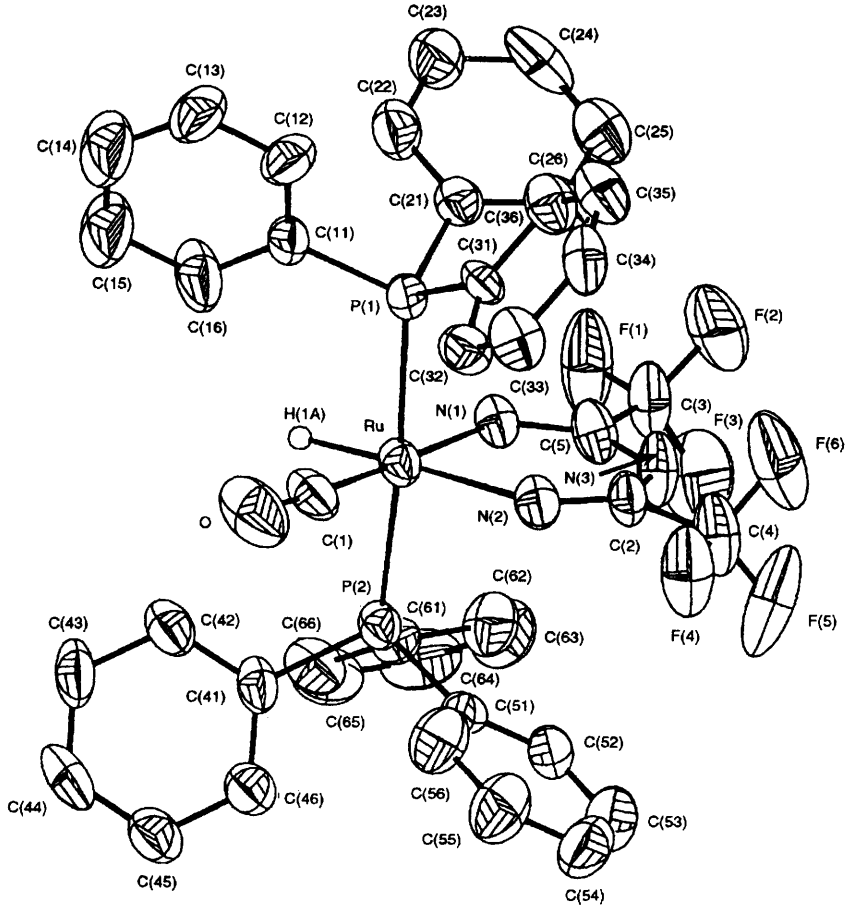


Fig. 1 Molecular structure and crystallographic numbering sequence for $[Ru\{NHC(CF_3)NC(CF_3)NH\}H(CO)(PPh_3)_2]$

long reaction time (17 h) employed only one trifluoroacetate group was replaced. Since the first trifluoroacetate ligand is known to be lost readily from $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$[11] it seems probable that the observed product can be obtained using much shorter reaction times. The NMR data (Table 1) are fully consistent with stereochemistry **III**. However marked broadening of one of the two ^{19}F NMR signals and one of the two infrared ν(N–H) stretching vibrations suggests the presence

Table 4 Selected bond lengths (Å) and angles (°) for [Ru{NHC(CF$_3$)NC(CF$_3$)NH}H(CO)(PPh$_3$)$_2$]

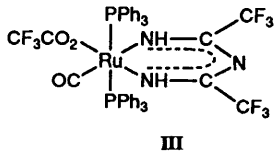
Ru–H(1A)	1.73(5)	Ru–C(1)	1.819(9)
Ru–N(1)	2.101(7)	Ru–N(2)	2.119(6)
Ru–P(1)	2.360(2)	Ru–P(2)	2.364(2)
F(1)–C(3)	1.306(10)	F(2)–C(3)	1.325(11)
F(3)–C(3)	1.316(12)	F(4)–C(4)	1.343(10)
F(5)–C(4)	1.294(12)	F(6)–C(4)	1.306(12)
P(1)–C(21)	1.831(4)	P(1)–C(11)	1.833(4)
P(1)–C(31)	1.832(4)	P(2)–C(51)	1.828(5)
P(2)–C(61)	1.834(4)	P(2)–C(41)	1.832(4)
N(1)–C(5)	1.295(10)	N(2)–C(2)	1.299(9)
N(3)–C(5)	1.309(10)	N(3)–C(2)	1.360(10)
O–C(1)	1.181(9)	C(5)–C(3)	1.542(12)
C(2)–C(4)	1.499(12)		
H(1A)–Ru–C(1)	85(2)	H(1A)–Ru–N(1)	93(2)
C(1)–Ru–N(1)	178.4(4)	H(1A)–Ru–N(2)	176(2)
C(1)–Ru–N(2)	98.4(3)	N(1)–Ru–N(2)	83.0(3)
H(1A)–Ru–P(1)	89(2)	C(1)–Ru–P(1)	89.1(3)
N(1)–Ru–P(1)	90.0(2)	N(2)–Ru–P(1)	92.7(2)
H(1A)–Ru–P(2)	88(2)	C(1)–Ru–P(2)	89.0(3)
N(1)–Ru–P(2)	91.8(2)	N(2)–Ru–P(2)	91.1(2)
P(1)–Ru–P(2)	175.91(7)		
C(21)–P(1)–Ru	116.4(2)	C(11)–P(1)–Ru	116.9(2)
C(31)–P(1)–Ru	114.3(2)	C(51)–P(2)–C(61)	107.0(3)
C(51)–P(2)–Ru	111.5(2)	C(61)–P(2)–Ru	117.0(2)
C(41)–P(2)–Ru	117.3(2)	C(5)–N(1)–Ru	128.6(6)
C(2)–N(2)–Ru	127.6(6)	C(5)–N(3)–C(2)	121.8(7)
O–C(1)–Ru	176.8(9)	N(1)–C(5)–N(3)	129.8(8)
N(1)–C(5)–C(3)	119.2(8)	N(3)–C(5)–C(3)	111.0(7)
N(2)–C(2)–N(3)	129.0(7)	N(2)–C(2)–C(4)	120.6(7)
N(3)–C(2)–C(4)	110.4(7)		

of intramolecular hydrogen bonding between the monodentate trifluoroacetate ligand and the adjacent NH moiety.

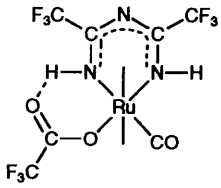
[Ru{NHC(CF$_3$)NC(CF$_3$)NH}$_2$(PPh$_3$)$_2$] **4**.—This complex was obtained in good yield as air-stable orange plates when [RuH(Cl)(PPh$_3$)$_3$] or [RuH$_2$(PPh$_3$)$_4$] was heated with the free amidine in boiling toluene. The *cis*-phosphine stereochemistry **IV** (M = Ru) was confirmed by the ^{13}C-{^{1}H} and ^{19}F NMR spectra (Table 1) which clearly establish the asymmetric environment of the NHC(CF$_3$)NC(CF$_3$)NH ligands. In yielding a bis(chelate) product of the form Ru(chelate ligand)$_2$(PPh$_3$)$_2$ the reaction of [RuH$_2$(PPh$_3$)$_4$] with NH=C(CF$_3$)–NH$_2$ parallels that between the same ruthenium complex and 1,3-diaryl triazenes R′N=N–NHR′.[12] However, it differs sharply from the reactions of [RuH$_2$(PPh$_3$)$_4$] with *N*,*N*′-diphenylamidines PhN=C(R)–NHPh which are accompanied by avid abstraction of CO from any available source and lead to the formation of the carbonylhydrido species [Ru{PhNC(R)NPh}H(CO)(PPh$_3$)$_2$] in modest yield.[2]

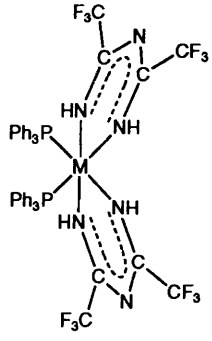
[Os{NHC(CF$_3$)NC(CF$_3$)NH}H(CO)(PPh$_3$)$_2$] **5**.—This product was obtained in good yield as air-stable yellow plates from the reaction of [OsH$_2$(CO)(PPh$_3$)$_3$] with the free amidine in boiling toluene. Spectroscopic data (Tables 1 and 2) are fully consistent with stereochemistry **I** (M = Os).

[Os{NHC(CF$_3$)NC(CF$_3$)NH}Cl(CO)(PPh$_3$)$_2$] **6a**, **6b**.—This product was obtained in two isomeric forms from the prolonged reaction of [OsH(Cl)(CO)(PPh$_3$)$_3$] with the free amidine in boiling toluene. The initial isomer **6a**, obtained after 16 h reflux, was shown by NMR spectroscopy to contain a symmetrically bound chelate ligand and was therefore assigned the *cis*-phosphine stereochemistry **IIa** (M = Os). Heating of this product in boiling toluene for 47 h yielded a 60:40 mixture of the *cis*-phosphine isomer **IIa** and the *trans* isomer **IIb** (M = Os).

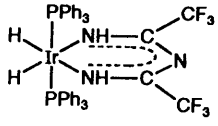


III





IV



V

[Os{NHC(CF$_3$)NC(CF$_3$)NH}$_2$(PPh$_3$)$_2$] **7**.—This product is obtained as air-stable dark orange-red microcrystals from the reaction of [OsH$_4$(PPh$_3$)$_3$] with free amidine in boiling toluene. Like its ruthenium analogue it displays NMR data consistent with the presence of asymmetrically located chelate ligands and is therefore assigned stereochemistry **IV** (M = Os). As in the case of the corresponding ruthenium complex (see above) there is no evidence for the formation of carbonyl-containing products.

[Ir{NHC(CF$_3$)NC(CF$_3$)NH}H$_2$(PPh$_3$)$_2$] **8**.—The reaction of *mer*-[IrH$_3$(PPh$_3$)$_3$] with free amidine in boiling toluene afforded the above product in good yield as air-stable yellow needles. The ^{1}H, ^{13}C-{^{1}H}, ^{19}F and ^{31}P-{^{1}H} NMR data are indicative of stereochemistry **V**. In particular the high-field proton triplet signal at δ −19.53 is consistent with the presence of a pair of hydride ligands *trans* to N-donors and *cis* to a pair of equivalent P-donors ($^2J_{HP}$ 17 Hz).

Carbon-13 *NMR Data for Triphenylphosphine Ligands*.—Phosphorus–carbon coupling patterns were used further to confirm stereochemical assignments. The ^{13}C-{^{1}H} resonances of the triphenylphosphine *o*-, *m*- and *p*-carbon atoms occur at *ca.* δ 133.5, 128.5 and 130 respectively. Their resonance frequencies and forms are independent of stereochemistry (*cis*/*trans* phosphines), resonances due to *o*- and *m*-carbons appear as triplets (J_{CP} *ca.* 4–6 Hz) whereas those due to the *p*-carbons are singlets. However, as anticipated, signals arising from carbons attached directly to phosphorus do display stereochemical sensitivity. Those associated with mutually *trans*-phosphorus nuclei appear as virtually coupled triplets (J_{CP} *ca.* 21–26 Hz) whereas those generated by carbons bound to mutually *cis*-phosphorus nuclei give rise to sharp doublets (separation *ca.* 48–53 hz) with a broad central hump.

Crystal Structure of [Ru{NHC(CF$_3$)NC(CF$_3$)NH}H(CO)(PPh$_3$)$_2$].—The molecular structure and crystallographic numbering sequence are shown in Fig. 1, and selected bond lengths and angles are presented in Table 4. The complex is essentially octahedral with metal–ligand bond distances typical for six-co-ordinate ruthenium(II). The most interesting feature is the Ru{NHC(CF$_3$)NC(CF$_3$)NH} metallocycle which is virtually planar with evidence of extensive electron delocalisation within the ring. Intraligand bond distances and angles are very similar to those previously reported[4] for the

identical metallocycle in the closely related complex $[Ru\{NHC(CF_3)NC(CF_3)NH\}\{P(OMe)_3\}(C_5H_5)]$. The only unexpected feature is the apparent asymmetry present in the $C^3F_3C^5N^3C^2C^4F_3$ moiety for which differences in lengths for the pair of CF_3–C bonds and the pair of C–N^3 bonds lie just outside the limits of experimental error. At present we have no explanation for this observation.

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