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Molecular iodoalkane complexes: preparation of the complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(IR)]PF_6$, $(R = CH_3, CH_2SiMe_3)$, and the crystal structures of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)I]$ and $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(ICH_3)]PF_6$

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Abstract

Reaction of the molecular hydrogen complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(\eta^2\text{-}H_2)]PF_6$ (**1**) with CH_3I and Me_3SiCH_2I leads to the iodoalkane complexes $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(IR)]PF_6$ ($R = CH_3$ (**2**) and $R = CH_2SiMe_3$ (**3**)), respectively. Treatment of the neutral iodide $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)I]$ (**4**) with $MeSO_3CF_3$ gave **2** as the triflate salt. The crystal structures of **2** and **4** have been determined.

Introduction

The coordination of haloalkanes to transition metal centres is of interest in the areas of metal based alkylation reagents and methanol feedstock chemistry [1]. Crabtree has reported examples of haloarene, haloalkane, and chelated fluoarene coordination via a halogen lone pair [2]. Gladyz [3] has recently reported the crystallographic characterisation of $[(\eta^5\text{-}C_5H_5)Re(PPh_3)(NO)(ICH_2SiMe_3)]BF_4$, while the only example of a crystallographically characterised iodomethane complex is the remarkable $[IrH_2(PPh_3)_2(ICH_3)_2]SbF_6$ [8]. We now report the preparation and crystal structure of the iodomethane complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(ICH_3)]PF6$ (**2**) and of a precursor, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)I]$ (**4**).

Results and discussion

The molecular hydrogen complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(\eta^2\text{-}H_2)]PF_6$ (**1**) which is formally d^6 Ru^{II} possesses a metal centre which is not sufficiently electron

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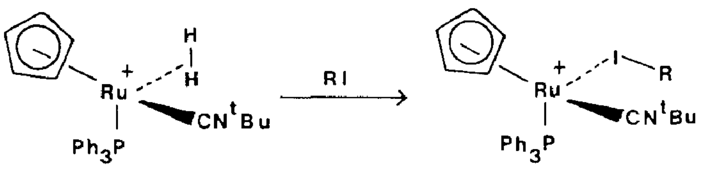
rich to induce oxidative addition of the hydrogen molecule [5], and so it was of interest to see whether it would react in this way with other simple molecules representing classical examples of oxidative addends. Reaction of iodomethane with **1** in CH_2Cl_2 solution rapidly gave a yellow solution from which yellow-orange microcrystals of **2** were isolated on addition of diethyl ether. The ^1H NMR spectrum of **2** in CD_2Cl_2 contains singlets at δ 4.84, 2.22 and 1.24 ppm due respectively to the C_5H_5, CH_3I, and ^tBu groups. The downfield shift of the methyl group relative to free iodomethane of 0.06 ppm is similar to that observed by Gladyz, but is in the opposite direction to the 0.99 ppm upfield shift seen for $[(\eta^5\text{-}C_5H_5)Ru(dppe)(ICH_3)]SO_2CF_3$. The absence of coupling of the methyl group to phosphorus indicates that no oxidative addition has occurred, for comparison in $[(\eta^5\text{-}C_5Me_5)Ru(PMe_3)_2(CH_3)(H)]BF_4$, the methyl resonance is at δ 0.13 with $J(PH)$ 9.5 Hz [6]. The dissolution of **2** in $(CD_3)_2CO$ causes slight shifts to low field of the three singlets to δ 5.09, 2.45 and 1.34 ppm, and also the appearance of a second set of resonances plus a singlet due to free iodomethane at δ 2.77 ppm. The second species present has been identified as a solvento complex $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(solv)]PF_6$ (**5a**) by in-situ synthesis from $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)I]$ (**4**) and silver perchlorate in acetone-d_6. Addition of CH_3I to this solution leads to immediate formation of **2**. A solvento complex **5b** could also be prepared in CD_2Cl_2, and exhibited singlets at δ 4.68 and 1.26 ppm for the C_5H_5 and ^tBu group, respectively.



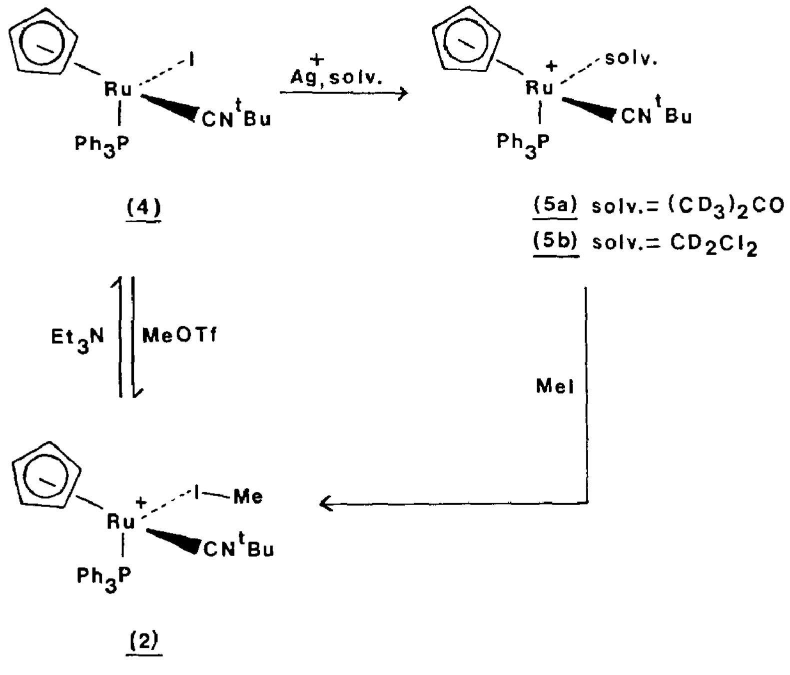
(1)

(2) R = Me

(3) R = CH_2SiMe_3

The resonance of the iodomethane ligand in the $^{13}C\{^1H\}$ spectrum occurs at δ -10.11, a downfield shift of 13.6 ppm relative to the free ligand, confirming the trend reported by Gladyz and Crabtree. Complex **3**, containing the Me_3SiCH_2I ligand was prepared by the reaction of **1** with the iodoalkane in CH_2Cl_2 and isolated as yellow-orange microcrystals in 81% yield. The ligand resonances in the ^1H NMR spectrum recorded in CD_2Cl_2 appeared at δ 2.10 and 0.13 ppm for the CH_2 and $SiMe_3$ groups, respectively, shifted downfield by 0.14 and 0.02 ppm relative to those for the free ligand. Both signals are singlets even though the methylene protons are diastereotopic, reflecting the remoteness of the asymmetric metal centre. The gated $^{13}C\{^1H\}$ spectrum contains a triplet at δ 2.69 ppm ($J(CH)$ 137 Hz) and a quartet at δ -1.84 ppm ($J(CH)$ 120 Hz) compared with values of δ -12.1 ($J(CH)$ 137 Hz) and δ -1.6 ($J(CH)$ 120 Hz) for the free ligand.

Complex **2** was also prepared by direct alkylation of **4** with $MeSO_3CF_3$ in dichloromethane; a similar reaction has also been observed by Crabtree [7]. We investigated this reaction by ^1H NMR spectroscopy and found that it is a stepwise process at 20 °C. Addition of ca. 1 equivalent of methyl triflate to a CD_2Cl_2 solution of **4** instantly produces the solvento species **5b**, free methyl iodide and a



small amount of **2**. The concentration of **2** increases over ca. 16 h until it is the only metal species in solution. Addition of an excess of methyl triflate does not affect the rate of transformation. These observations are best rationalised in terms of same ionisation of **4** in CD_2Cl_2 (to a degree below that detectable by ^1H NMR spectroscopy which goes rapidly to completion upon addition of $MeSO_3CF_3$. The free iodomethane produced slowly displaces the solvent from the coordination sphere of **5b** to produce **2**. We note that Crabtree's reaction of $[(\eta^5\text{-}C_5H_5)Ru(Ph_2PCH_2CH_2PPh_2)I]$ with $MeSO_3CF_3$ was carried out during 10–16 h, suggesting a common reaction pathway with that observed here [7]. The conductivity of a 3.9 m*M* solution of **4** in CH_2Cl_2 was 0.23 $cm^2\ mol^{-1}\ \Omega^{-1}$ at 21°C, compared to a value of 41.45 $cm^2\ mol^{-1}\ \Omega^{-1}$ for 4.0 m*M* solution of the salt $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(SMe_2)]PF_6$, suggesting that **4** is $\leqslant 0.5\%$ ionised in dichloromethane. The observations clearly rule out direct alkylation of either the iodide ligands or the ruthenium centre, since in the latter case iodomethane would be reductively eliminated from the coordination sphere and subsequently brought back into the coordination sphere as a donor ligand.

Addition of triethylamine to solutions of **2** in CH_2Cl_2 gave quantitative yields of **4** on work up. Monitoring of this reaction by ^1H NMR spectroscopy showed the reaction to be very clean, the only products being **4** and methyltriethylammonium cation.

Reaction of **2** with carbon monoxide (1–3 atm) gave a quantitative yield of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(CO)]PF_6$ (**6**), demonstrating the poor ligating ability of the iodomethane ligand.

X-ray structure of 2 *

Yellow-orange needles were obtained by crystallisation from a dichloromethane-diethyl ether solution. A suitable crystal was sealed into a Lindmann tube under nitrogen. Intensity data were obtained on a Nicolet R3m/V diffractometer using graphite monochromatized Mo-K_α X-rays.

Crystal data. $C_{29}H_{32}INP_2F_6Ru$, $M = 798.53$, orthorhombic, space group *Pbca* (No. 61), a 15.390(5) b 17.349(5) c 23.642(8) Å, U 6312(4) $Å^3$ D_c 1.68 g cm^{-3} for $Z = 8$, $F(000) = 3152$, $\mu(\text{Mo-}K_\alpha)$ 16.09 cm^{-1} $T = 23°C$, crystal size $0.47 \times 0.22 \times 0.10$ mm. Cell dimensions were obtained from 23 centred reflections with 2θ values from 15° to 28°. Intensity data in the range $3° < 2\theta < 50°$ were collected by a θ–2θ scan technique. The intensities of four relections measured periodically showed a decrease of 4% during the data collection. An empirical absorption correction was applied using an azimuthal scan technique.

A total of 6386 reflections were measured, 5215 unique, and 1702 for which $I > 3.0\sigma(I)$ were used in the refinement.

The structure was solved using standard heavy atom routines and refined using full matrix least squares methods. The ruthenium, iodine and phosphorus atoms were given anisotropic thermal parameters. The phenyl and cyclopentadienyl rings were refined as rigid bodies. Hydrogen atoms were placed in the model in calculated positions but not refined. There was considerable disorder in the PF_6^- group. An attempt was made to allow for this by constructing two PF_6 octahedra around a common phosphorus with occupancies of 60 and 40%, respectively. The PF_6 groups were restrained to be regular octahedra with refinable P–F distances. The highest peaks in the final difference map were less than 1 $eÅ^{-3}$ and were associated with the PF_6 group. At convergence $R = 6.36\%$ and $R_w = 6.43\%$ $w = [\sigma^2(F) + 0.00138 F^2]^{-1}$, $S = 1.32$ for 210 parameters, $\Delta/\sigma < 0.12$.

Calculations were performed by use of SHELXTL-PLUS. The final positional parameters are given in Table 1, and selected bond lengths and angles are given in Table 2.

X-ray structure of 4

Red needles were obtained by crystallisation from dichloromethane light petroleum ether (40–60 °C). A suitable crystal was mounted on a glass fibre with epoxy resin. Precession photographs and intensity data were collected on a Nicolet R3m/V diffractometer using graphite monochromatized Mo-Kα X-rays.

Crystal data. $C_{28}H_{29}INPRu$, $M = 638.52$, monoclinic, space group $P2_1/a$ (non-standard No. 14), a 9.751(4) b 17.194(7) c 15.751(6) Å, β 99.13(3)°, U-2607(2) $Å^3$, D_c 1.63 g cm^{-3} for $Z = 4$, $F(000) = 1264$, $\mu(\text{Mo-}K_\alpha)$ 18.09 cm^{-1}, T 23°C, crystal size $0.20 \times 0.12 \times 0.10$ mm. Cell dimensions were obtained from 28 centred reflections with 2θ values from 21° to 46°. Intensity data in the range $3° < 2\theta < 50°$ were collected using a θ–2θ scan technique. The intensities of three reflections measured periodically showed a decrease of 4% over the data collection. An empirical absorption correction was applied using an azimuthal scan technique. A

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* Tables of thermal parameters and lists of observed and calculated structure factors are available from the authors.

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**

	x	y	z	U_{eq} [a]
Ru(1)	797(1)	1584(1)	913(1)	39(1)
C(1)	−236(8)	2448(7)	1088(6)	66(6)
C(2)	−325	2165	527	45(5)
C(3)	−497	1362	558	65(6)
C(4)	−515	1149	1138	87(7)
C(5)	−354	1820	1465	70(7)
I(1)	1445(1)	175(1)	746(1)	61(1)
C(6)	1982(16)	−156(15)	1548(11)	93(7)
C(7)	1525(13)	1774(11)	1554(9)	47(5)
N(1)	1938(11)	1893(10)	1950(9)	55(5)
C(41)	2287(15)	2065(14)	2510(12)	73(7)
C(42)	2949(17)	2645(16)	2476(13)	115(8)
C(43)	1532(17)	2277(16)	2891(13)	113(8)
C(44)	2634(18)	1293(17)	2733(13)	123(9)
P(1)	1830(3)	2124(3)	312(2)	34(2)
C(11)	1595(11)	3115(10)	113(8)	33(5)
C(12)	1260(12)	3630(11)	502(10)	50(5)
C(13)	1082(12)	4369(13)	358(11)	56(6)
C(14)	1187(14)	4607(15)	−200(11)	73(7)
C(15)	1533(15)	4133(14)	−593(12)	83(7)
C(16)	1721(12)	3375(12)	−441(10)	53(5)
C(21)	1977(12)	1633(11)	−349(8)	38(5)
C(22)	1257(13)	1292(12)	−612(10)	54(6)
C(23)	1361(14)	917(12)	−1112(10)	61(6)
C(24)	2127(14)	861(12)	−1401(11)	62(6)
C(25)	2837(14)	1152(13)	−1135(10)	60(6)
C(26)	2771(12)	1554(11)	−618(9)	48(5)
C(31)	2916(11)	2182(10)	616(9)	36(5)
C(32)	3391(12)	1513(12)	696(9)	54(5)
C(33)	4183(15)	1587(14)	952(10)	69(6)
C(34)	4546(15)	2256(14)	1113(11)	69(6)
C(35)	4099(13)	2919(12)	1028(9)	53(6)
C(36)	3273(12)	2889(12)	766(9)	52(6)
P(2)	4934(4)	−363(4)	2181(3)	81(3)
F(1)	5939(7)	−450(13)	2213(10)	115(8)
F(2)	4854(14)	−1220(8)	1994(11)	166(10)
F(3)	4861(16)	−613(16)	2811(6)	295(13)
F(4)	5015(14)	494(8)	2368(11)	169(10)
F(5)	5008(16)	−113(16)	1551(5)	252(12)
F(6)	3929(7)	−276(13)	2150(10)	206(11)
F(11)	5052(17)	−663(17)	1566(6)	125(10)
F(21)	4073(12)	−827(16)	2233(12)	155(12)
F(31)	5450(18)	−1069(12)	2408(12)	167(12)
F(41)	5796(12)	101(16)	2130(12)	169(12)
F(51)	4419(18)	344(12)	1954(12)	165(12)
F(61)	4816(17)	−63(17)	2797(6)	144(11)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

total of 4793 reflections were collected, and 2850 for which $I > 2\sigma(I)$ were used in the refinement. The structure was solved by standard heavy atom routines and refined by full matrix least squares methods. All non-hydrogen atoms were given

Table 2

Selected bond lengths (Å) and bond angles (°) for **2**

Ru(1)–C(1)	2.224 (12)	Ru(1)–C(2)	2.198 (13)
Ru(1)–C(3)	2.195 (13)	Ru(1)–C(4)	2.221 (13)
Ru(1)–C(5)	2.239 (13)	Ru(1)–I(1)	2.670 (2)
Ru(1)–C(7)	1.913 (21)	Ru(1)–P(1)	2.328 (6)
I(1)–C(6)	2.146 (26)	C(7)–N(1)	1.150 (29)
N(1)–C(41)	1.461 (34)		
		I(1)–Ru(1)–C(7)	93.2(6)
I(1)–Ru(1)–P(1)	91.3(1)	C(7)–Ru(1)–P(1)	90.9(6)
Ru(1)–I(1)–C(6)	104.9(7)	Ru(1)–C(7)–N(1)	177.8(19)
C(7)–N(1)–C(41)	168.0(21)		

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters for **4** ($Å^2 \times 10^3$)

	x	y	z	U_{eq} [a]
Ru(1)	1487(1)	454(1)	1687(1)	38(1)
I(1)	−719(1)	−420(1)	1984(1)	58(1)
C(1)	2423(15)	1490(7)	1235(9)	70(5)
C(2)	1582(20)	1134(8)	546(8)	80(6)
C(3)	268(19)	1152(9)	662(10)	87(6)
C(5)	224(16)	1525(8)	1434(11)	79(6)
C(5)	1532(20)	1732(7)	1784(7)	76(6)
P(1)	2741(3)	212(1)	3011(2)	36(1)
C(11)	1957(11)	414(6)	3973(5)	42(3)
C(12)	957(12)	988(6)	3935(6)	43(3)
C(13)	437(12)	1199(6)	4668(6)	51(4)
C(14)	849(13)	828(6)	5437(6)	51(4)
C(15)	1840(13)	258(6)	5465(6)	53(4)
C(16)	2403(11)	41(6)	4739(6)	54(4)
C(21)	3468(11)	−780(6)	3238(6)	39(3)
C(22)	4811(12)	−879(6)	3636(6)	50(4)
C(23)	5329(14)	−1625(7)	3784(7)	59(5)
C(24)	4556(15)	−2255(7)	3547(8)	66(5)
C(25)	3207(14)	−2149(7)	3153(8)	64(5)
C(26)	2645(13)	−1414(6)	3005(7)	54(4)
C(31)	4310(11)	816(5)	3196(6)	38(3)
C(32)	4611(12)	1310(6)	3888(6)	47(4)
C(33)	5813(14)	1743(6)	3988(8)	66(5)
C(34)	6724(14)	1705(7)	3415(8)	64(5)
C(35)	6441(13)	1180(7)	2727(7)	60(4)
C(36)	5216(12)	756(6)	2613(6)	51(4)
C(41)	2442(11)	−391(6)	1263(6)	45(4)
N(1)	3060(11)	−866(6)	963(6)	62(4)
C(42)	3981(13)	−1415(7)	651(7)	54(4)
C(43)	5331(16)	−1345(11)	1201(11)	133(9)
C(44)	3354(22)	−2193(8)	767(12)	149(11)
C(45)	4041(20)	−1281(11)	−262(9)	138(10)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 4

Selected bond lengths (Å) and bond angles (°) for **4**

Ru(1)-I(1)	2.724 (1)	Ru(1)-C(1)	2.172 (13)
Ru(1)-C(2)	2.158 (13)	Ru(1)-C(3)	2.202 (15)
Ru(1)-C(4)	2.215 (14)	Ru(1)-C(5)	2.202 (12)
Ru(1)-P(1)	2.282 (2)	Ru(1)-C(41)	1.904 (11)
C(41)-N(1)	1.159 (15)	N(1)-C(42)	1.442 (16)
I(1)-Ru(1)-P(1)	93.8(1)	I(1)-Ru(1)-C(41)	94.8(3)
P(1)-Ru(1)-C(41)	87.7(3)	Ru(1)-C(41)-N(1)	174.8(10)
C(41)-N(1)-C(42)	172.8(11)		

anisotropic temperature factors. Hydrogen atoms were placed in the model in calculated positions but were not refined. The highest peaks in the final difference map were less than 0.8 e$Å^{-3}$ and associated with the iodine atom. At convergence $R = 5.80\%$ and $R_w = 5.21\%$, $w = [\sigma^2(F) + 0.0002F^2]^{-1}$, $S = 1.52$ for 289 parameters, $\Delta/\sigma < 0.001$. Calculations were performed using SHELXTL-PLUS. The final positional parameters are given in Table 3, and selected bond lengths are given in Table 4.

Discussion of the solid state structures 2 and 4

The molecular structures of **2** and **4** are shown in Fig. 1 and 2, respectively. Both compounds show pseudo-octahedral coordination geometry with the cyclopentadientyl group occupying three sites in a *fac*-arrangement. The iodomethane ligand in **2** is orientated in such a way that the methyl group is pointing towards the isonitrile group in an "internal" arrangement, and further the methyl group is pointing out of the plane defined by I(1), Ru(1) and C(7) towards the cyclopentadienyl group, so that the plane Ru(1), I(1), C(6) is at 21° to that plane. The bond

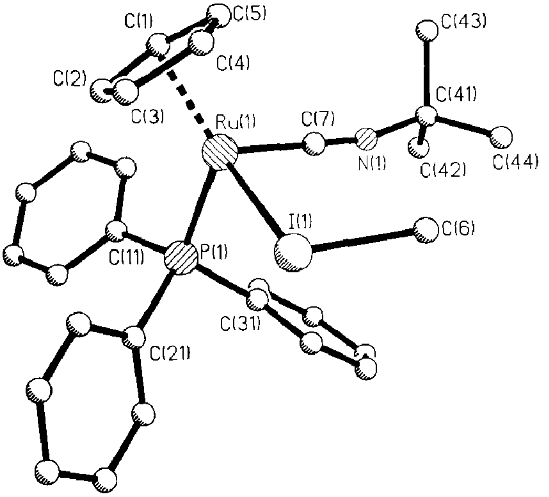

Fig. 1. Proposed molecular structure for $(C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)(ICH_3)]PF_6$ (**2**).

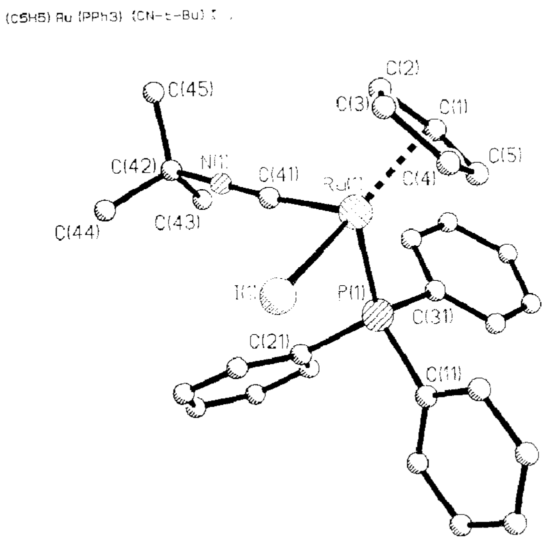

Fig. 2. Proposed molecular structure for $(C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)I$ (4).

angle at I(1) of 104.9(7)° compares with angles of 105.5 and 108.2° for the two iodomethane ligands in $[IrH_2(PPh_3)_2(ICH_3)_2]SbF_6$ [4]. Similarly the bond length I(1)–C(6) of 2.146(26) Å compares with 2.13(1) and 2.12(2) Å for the C–I distance in that complex. The bond length in free iodomethane [8] is 2.1387 Å but the error limits for **2** do not allow discussion of hybridisation changes at iodine on coordination to the metal centre. The effects at the carbon atom attached to iodine are certainly small since for complex **3** no changes in $^1J(CH)$ are observed on coordination. The "internal" arrangement of the methyl group in **2** can be simply rationalised in terms of VSEPR theory; the lone pairs on iodine cannot be accommodated near the isonitrile group.

Comparison of the coordination spheres of **2** and **4** shows some interesting features, since although the ruthenium-iodine bond shortens by 0.054 Å on going from **4** to **2**, the ruthenium–phosphorus bond lengthens by 0.046 Å while the ruthenium–isonitrile bond is unchanged. This is in accordance with the positive charge in **2** being associated with the iodomethane ligand, and the ease with which Me^+ can be removed from **2** by base supports this suggestion.

Experimental

All reactions and preparations were carried out under nitrogen by standard Schlenk-tube techniques. Tetrahydrofuran was dried over sodium benzophenone ketyl and distilled. Diethyl ether and light petroleum (b.p. 40–60 °C) were dried over sodium wire and distilled. Dichloromethane was dried over phosphorus pentoxide and distilled. All other solvents were used as supplied. Reactions performed at > 1 atm pressure were carried out in Fischer–Porter bottles. Infrared spectra were recorded on a Perkin–Elmer 1710 FTIR instrument. Nuclear magnetic resonance spectra were recorded on Perkin–Elmer R32 (90 MHz, ^1H) and Bruker AC300 (300.13 MHz, ^1H; 121.49 MHz, ^{31}P; 75.47 MHz, ^{13}C) spectrometers. Elemental analyses were by Butterworth Laboratories, London. Iodomethane was allowed to stand over copper powder prior to use and (iodomethyl)trimethylsilane was used as supplied (Aldrich). The compounds **1** and [(η^5-C_5H_5)Ru(PPh)$_3$(CN^{t}Bu)Cl] were prepared as described previously [5].

[(η^5-C_5H_5)Ru(PPh_3)(CN^{t}Bu)(ICH_3)]PF_6 (2)

Iodomethane (1 ml, excess) was added to a solution of **1** (0.20 g, 0.2 mmol) in CH_2Cl_2 (30 ml) and the mixture was stirred (20 °C) for 4 h. Filtration, concentration (to ca. 10 ml), and addition of diethyl ether (30 ml) gave yellow-orange crystals, yield 0.21 g (88%), (Found: C, 43.54; H, 4.07; N, 1.45. $C_{29}H_{32}F_6INP_2Ru$ calcd.: C, 43.62; H, 4.04; N, 1.75%). IR (Nujol): ν_{max} 2154s cm^{-1} (CN); ^1H NMR (CD_2Cl_2): δ 7.50 and 7.28 (m, 15H, Ph), 4.84 (s, 5H, C_5H_5), 2.22 (s, 3H, CH_3), 1.24 (s, 9H, CMe_3) ppm; ^1H NMR ($(CD_3)_2CO$): δ 7.57 (m, 15H, Ph), 5.09 (s, 5H, C_5H_5), 2.45 (s, 3H, CH_3), 1.34 (s, 9H, CMe_3) ppm; $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 136.17 (d, J(PC) 46.7 Hz, C_{ipso}), 134.33 (d, J(PC) 10.8 Hz, C_{ortho}), 131.23 (s, C_{para}), 129.40 (d, J(PC) 11.2 Hz, C_{meta}), 80.57 (s, C_5H_5), 58.78 (s, $CNCMe_3$), 30.42 (s, $CNC\mathit{Me}_3$), −10.11 (s, CH_3) ppm; $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 49.7 ppm.

[(η^5-C_5H_5)Ru(PPh_3)(CN^{t}Bu)(ICH_2SiMe_3)]PF_6 (3)

(Iodomethyl)trimethylsilane (0.5 ml, excess) was added to a solution of **1** (0.15 g, 0.23 mmol) in dichloromethane (20 ml) and the mixture was stirred (20 °C) for 3 h. Filtration, concentration (to ca. 12 ml), and addition of diethyl ether (30 ml) gave orange crystals, yield 0.16 g (81%). (Found: C, 43.88; H, 4.71; N, 1.68. $C_{32}H_{40}F_6INP_2SiRu$ calcd.: C, 44.14; H, 4.63; N, 1.61%). IR (Nujol): ν_{max} 2158s cm^{-1} (CN); ^1H NMR (CD_2Cl_2): δ 7.48 and 7.29 (m, 15H, Ph), 4.84 (s, 5H, C_5H_5), 2.10 (s, 2H, CH_2), 1.24 (s, 9H, CMe_3), 0.13 (s, 9H, $SiMe_3$ ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 135.3 (d, J(PC) 48 Hz, C_{ipso}), 133.6 (d, J(PC) 10.6 Hz, C_{ortho}), 131.1 (s, C_{para}), 129.1 (d, J(PC) 9 Hz, C_{meta}), 82.7 (s, C_5H_5), 58.7 (s, $\mathit{C}Me_3$), 30.5 (s, $C\mathit{Me}_3$), 2.69 (s, CH_2), −1.84 (s, $Si\mathit{Me}_3$) ppm; $^{31}P\{^1H\}$ NMR (CH_2Cl_2): δ 54.2 ppm.

[(η^5-C_5H_5)Ru(PPh_3)(CN^{t}Bu)I] (4)

Sodium iodide (0.3 g, 2 mmol) was added to a solution of [(η^5-C_5H_5)Ru(PPh_3)(CN^{t}Bu)Cl] (0.25 g, 0.46 mmol) in acetone (30 ml). The mixture was stirred at 20 °C for 24 h, then evaporated to dryness under reduced pressure. Extraction of the residue with dichloromethane (2 × 30 ml) followed by concentration of the filtrate (to ca. 15 ml) and addition of petroleum ether (40 ml) gave red crystals, yield 0.16 g (54%). (Found: C, 52.95; H, 4.60; N, 2.18. $C_{28}H_{29}INPRu$ calcd.: C, 52.67; H, 4.58; N, 2.19%). IR (Nujol): 2106 s cm^{-1} (CN); ^1H NMR ($CDCl_3$): δ 7.49 and 7.31 (M, 15H, Ph), 4.54 (s, 5H, C_5H_5), 1.15 (s, 9H, CMe_3) ppm; ^1H NMR (CD_2Cl_2): δ 7.52 and 7.37 (m, 15H, Ph), 4.57 (s, 5H, C_5H_5), 1.19 (s, 9H, CMe_3) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.8 (d, J(PC) 43.8 Hz, C_{ipso}), 134.0 (d, J(PC) 10.5 Hz, C_{ortho}), 129.4 (s, C_{para}), 127.7 (d, J(PC) 9.8 Hz, C_{meta}), 81.9 (s, C_5H_5), 30.9 (s, $C\mathit{Me}_3$) ppm.

The conductivity of **4** as a 3.9×10^{-4} *M* solution in CH_2Cl_2 was 0.23 cm^2 mol^{-1} Ω^{-1} at 21 °C.

[(η^5-C_5H_5)Ru(PPh_3)(CN^{t}Bu)(solvent)]ClO_4 (5a, 5b)

(a) Solvent $(CD_3)_2CO$. Acetone-d_6 (0.7 ml) was added to a mixture of **4** (20 mg) and $AgClO_4$ (10 mg) in an NMR tube. The clear yellow supernatant solution was examined by ^{1}H NMR: δ 7.57 (m, 15H, Ph), 4.87 (s, 5H, C_5H_5), 1.31 (s, 9H, CMe_3) ppm and $^{13}C\{^{1}H\}$ NMR: δ 135.13 (d, J(PC) 44.9 Hz, C_{ipso}, 134.18 (d, J(PC) 11 Hz, C_{ortho}),m 131.48 (s, C_{para}), 129.56 (d, J(P) 11.9 Hz, C_{meta}), 83.29 (s, C_5H_5), 59.08 (s, CMe_3), 30.87 (s, CMe_3) ppm.

Addition of iodomethane (4 μl) to the solution and re-examination by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy showed the presence of **2** and free iodomethane (δ 2.17 ppm (^{1}H) and δ -23.68 ppm (^{13}C)].

(b) solvent CD_2Cl_2. In a procedure similar to that above, the ^{1}H NMR spectrum of this solvento species was obtained: δ 7.39 (m, 15H, Ph), 4.68 (s, 5H, C_5H_5), 1.26 (s, 9H, CMe_3) ppm. Also the $^{31}P\{^{1}H\}$ spectrum: δ 50.6 ppm.

Addition of iodomethane cleanly generated a solution of **2**, and a singlet was observed for free ligand at δ 2.16 ppm.

*Reaction of **2** with triethylamine*

Triethylamine (0.2 ml) was added to a solution of **2** (0.2 g, 0.25 mmol) in dichloromethane (25 ml). The orange solution darkened immediately and was stirred for 12 h. The solvent was removed under reduced pressure and the residue washed with diethyl ether (20 ml). Extraction of the solid with dichloromethane (2 × 10 ml), concentration, and addition of light petroleum ether have red crystals of **4**, 0.13 g (80%), which were identified by IR and ^{1}H NMR spectroscopy.

Repetition of the experiment on a reduced scale with monitoring by ^{1}H NMR spectroscopy showed clean rapid conversion of **2** to **4**, and the appearance of Et_3MeNPF_6, characterised by ^{1}H NMR spectroscopy: CD_2Cl_2 δ 3.272 (q, 6H, ^{3}J(HH) 7 Hz, CH_2), 2.920 (s, 3H, NCH_3), 1.355 (tt, 9H, ^{3}J(HH) 7 Hz, ^{3}J(NH) 2 Hz, CH_3) ppm.

*$[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)(CO)]PF_6$ (**6**)*

A suspension of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN^tBu)Cl]$ (0.21 g, 0.38 mmol) and NH_4PF_6 (0.12 g, 0.76 mmol) in methanol (30 ml) was stirred under a CO atmosphere (80 psi) at 70 °C for 3 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (30 ml). Concentration (to 10 ml) and slow addition of diethyl ether (30 ml) with stirring gave white microcrystals, yield 0.22 g (84%). (Found: C, 50.51; H, 4.22; N, 2.18. $C_{29}H_{29}F_6NOP_2Ru$ calcd.: C, 50.88; H, 4.27; N, 2.05%. IR (Nujol): 2186s (CN), 2014s (CO) cm^{-1}; ^{1}H NMR ($(CD_3)_2CO$): δ 7.73–7.29 (m, 15H, Ph), 5.57 (s, 5H, C_5H_5), 1.29 (s, 9H, CMe_3) ppm; $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2 δ 47.5 ppm.

*Reaction of **2** with carbon monoxide*

A solution of **2** (0.3 g, 0.38 mmol) in dichloromethane (20 ml) was stirred under a CO atmosphere (80 psi) at 20 °C for 2 h. Concentration and addition of diethyl ether gave white microcrystalline **6** 0.24 g (95%) identified by IR and ^{1}H NMR spectroscopy.

*Reaction of **4** with $CH_3SO_3CF_3$*

The reaction was monitored by ^{1}H NMR spectroscopy in situ. Addition of ca. 0.6 equivalents of $CH_3SO_3CF_3$ to a solution of **4** in CD_2Cl_2 led to immediate and complete consumption of the reagent and formation of **2** and the solvento species **5b** in the ratio 1/18 along with free iodomethane.

A separate experiment in which an excess of $CH_3SO_3CF_3$ (> 10 equiv.) was used produced the same initial result, and monitoring during 18 h showed the build-up of **2** and the concurrent loss of free iodomethane and the solvento species. The conversion of **4** onto **2** was complete after 16 h at 22° C.

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