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Ruthenium clusters with nitrogen ligands IV [☆]. Double C–H activation of ketimine methyl groups on triruthenium carbonyl clusters. Crystal structure of $Ru_3(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}(N,C)\text{-}4\text{-}HOC_6H_4N{=}CMeCH](CO)_9 .\ Et_2O$

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Abstract

The reaction of $Ru_3(CO)_{12}$ with the Schiff base 4-hydroxyphenyl-*N,N*-dimethylimide in refluxing cyclohexane gave the title complex in excellent yield. An X-ray crystallographic study showed that the product is derived from an unusual double C–H activation of the methyl group. An analogous reaction with the asymmetric Schiff base *p*-hydroxyphenyl-*N,N*-isobutylmethylimide showed that this reaction is specific for the imine-bound methyl group.

Keywords: Ruthenium; Carbonyl; Ketoimine; Crystal structure; Fluxionality

1. Introduction

The chemistry of metal clusters with organic substrates has been the subject of intense interest [2], with $Os_3(CO)_{12}$ and its derivatives the most extensively investigated [3,4]. As part of these studies, a wide variety of *N*-ligands have been employed on both the triosmium system [3,4] and the related triruthenium system [15], to the extent that reactivity patterns and bonding modes are becoming predictable. To the best of our knowledge, however, the Group 8 cluster chemistry of Schiff bases is restricted to two activated ligand types: aldimines [6–9], where imine C–H oxidative addition across an M–M bond occurs very readily, and α,β-unsaturated imines [10], which react by way of a facile intraligand hydrogen shift. We now report that reactions of $Ru_3(CO)_{12}$ with ketimines bearing aliphatic substituents, $4\text{-}HOC_6H_4N{=}CMe_2$ or $4\text{-}HOC_6H_4\text{-}N{=}C^iBuMe$, proceed by imine coordination and an unusual double C–H activation of a methyl group; the product of the former reaction, $Ru_3(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}(N,C)\text{-}4\text{-}HOC_6H_4N{=}CMeCH](CO)_9$ (**1**), has been fully characterized by an X-ray structural study.

2. Results and discussion

2.1. Synthesis and spectroscopic characterization of 1

A mixture of 4-hydroxyphenyl-*N,N*-dimethylimide and $Ru_3(CO)_{12}$ in cyclohexane was refluxed for 22 h. Work-up afforded the title complex $Ru_3(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}(N,C)\text{-}4\text{-}HOC_6H_4N{=}CMeCH](CO)_9$ (**1**) as a yellow powder in excellent yield. The product was characterized by a combination of IR, ^1H and ^{13}C NMR spectroscopies, FAB MS, microanalyses, and an X-ray diffraction study. The IR spectra indicate that the hydroxy function of the organic precursor is retained and that the cluster carbonyl ligands all occupy terminal sites. The ^1H NMR spectrum contains signals assigned to a *para*-substituted aromatic ring, a hydroxy unit, and one methyl

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[☆] For Part III, see Ref. [1].

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group; the second methyl group of the precursor has been replaced by two hydrido ligands and a CH moiety. At 238 K, the ^{13}C NMR spectrum contains signals assigned to imino C, nine carbonyl resonances, aryl C, and methyl and methylidyne groups. Broadening and coalescence in the carbonyl and aryl regions are apparent at higher temperatures (see below). The FAB mass spectrum contains no molecular ion, the peak at highest mass corresponding to loss of one carbonyl ligand. As the spectral data did not allow us to assign the molecular structure of **1** unambiguously an X-ray diffraction study was carried out.

2.2. X-ray structural study of 1

The molecular structure of **1** was determined by a single-crystal X-ray study. A summary of the crystal and refinement data is found in Table 1, fractional coordinates of non-hydrogen atoms are given in Table 2, and selected bond distances and angles are listed in Table 3. An ORTEP plot showing the molecular geometry and atomic numbering scheme is shown in Fig. 1.

Complex **1** retains the Ru_3 triangular framework of the precursor cluster $Ru_3(CO)_{12}$, and possesses three terminal carbonyls attached to each ruthenium, two edge-bridging hydrido ligands and a face-capping ketimine residue. One Ru_3 core distance [Ru(1)–Ru(2) 2.985(1) Å] is significantly longer than the other two [2.7823(8), 2.8002(8) Å], which is consistent with the presence of an edge-bridging hydrido ligand located in the refinement. The other hydride was located as bridging Ru(2)–Ru(3), with the bond lengthening usually associated with edge-bridging hydrides precluded by the bridging alkylidene. Ru–CO interactions fall into two distinct groups; six are in the range 1.893(4)–1.909(4) Å, with two of the longer distances Ru(2)–C(23) 1.954(4) Å, Ru(3)–C(33) 1.934(4) Å, being associated with carbonyls *trans* to the metal–alkylidene interactions; the remaining long Ru–CO, Ru(1)–C(12) 1.947(4) Å, is *trans* to Ru(1)–Ru(3). Ru–C–O angles for these carbonyls are essentially linear, being in the range 176–179°, with no significant semibridging interactions. The Schiff base residue is coordinated to the cluster by an *N*-donor interaction to Ru(1) [Ru(1)–N(01) 2.134(3) Å] and an alkylidene symmetrically bridging Ru(2) and Ru(3) [Ru(2)–C(012) 2.150(3) Å, Ru(3)–C(012) 2.135(3) Å]. The imino linkage [N(01)–C(011) 1.301(4) Å] is consistent with an N=C interaction, C(011)–C(012) 1.451(5) Å is normal for a C(sp^2)–C(sp^3) distance, and all distances associated with the *p*-hydroxyphenyl group are also not unusual. The Schiff base

Table 1
Summary of crystallographic data for **1**

Formula	$C_{22}H_{21}NO_{11}Ru_3$
M	778.6
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	12.923(4)
b (Å)	10.803(5)
c (Å)	10.035(4)
α (°)	82.91(4)
β (°)	86.76(3)
γ (°)	88.68(3)
V (Å^3)	1388(1)
$D_{\text{calc.}}$ (g cm^{-3})	1.86
Z	2
μ_{Mo} (cm^{-1})	16.7
Specimen (mm^3)	0.24×0.38×0.65
$A^*_{\text{min,max}}$	1.54, 1.77
$2\theta_{\text{max}}$(°)	60
N	7898
N_o	6121
R	0.031
R_w	0.035

Table 2
Non-hydrogen atom coordinates and equivalent isotropic displacement parameters for **1**

Atom	x	y	z	U_{eq} Å^2
Ru(1)	0.34315(2)	0.39084(2)	0.81199(3)	0.03945(8)
Ru(2)	0.27967(2)	0.42647(3)	0.52821(3)	0.04158(9)
Ru(3)	0.15400(2)	0.30828(3)	0.74055(3)	0.04112(9)
C(11)	0.3089(3)	0.3321(4)	0.9958(4)	0.053(1)
O(11)	0.2911(3)	0.2966(3)	1.1056(3)	0.081(1)
C(12)	0.4786(3)	0.4577(3)	0.8359(3)	0.045(1)
O(12)	0.5593(2)	0.4900(3)	0.8479(3)	0.065(1)
C(13)	0.3982(3)	0.2316(4)	0.7808(4)	0.054(1)
O(13)	0.4306(2)	0.1382(3)	0.7589(3)	0.081(1)
C(21)	0.3298(3)	0.5854(4)	0.4529(4)	0.061(1)
O(21)	0.3609(3)	0.6787(3)	0.4090(4)	0.098(2)
C(22)	0.1836(3)	0.4233(4)	0.3910(4)	0.056(1)
O(22)	0.1245(3)	0.4235(3)	0.3128(3)	0.086(1)
C(23)	0.3875(3)	0.3283(4)	0.4432(4)	0.059(1)
O(23)	0.4495(3)	0.2711(3)	0.3958(4)	0.097(2)
C(31)	0.0269(3)	0.2887(4)	0.6584(4)	0.058(1)
O(31)	−0.0501(2)	0.2817(3)	0.6106(3)	0.092(1)
C(32)	0.0930(3)	0.3482(4)	0.9062(4)	0.054(1)
O(32)	0.0550(2)	0.3728(3)	1.0044(3)	0.083(1)
C(33)	0.1773(3)	0.1325(4)	0.7964(4)	0.057(1)
O(33)	0.1896(3)	0.0291(3)	0.8251(4)	0.087(1)
C(01)	0.2908(2)	0.6556(3)	0.9081(3)	0.041(1)
C(011)	0.1895(2)	0.5912(3)	0.7397(3)	0.040(1)
C(012)	0.1598(3)	0.4994(3)	0.6556(3)	0.043(1)
C(013)	0.1317(4)	0.7135(4)	0.7296(5)	0.058(1)
N(01)	0.2635(2)	0.5650(2)	0.8216(3)	0.0415(8)
C(02)	0.2331(3)	0.6661(4)	1.0271(4)	0.049(1)
C(03)	0.2542(3)	0.7595(4)	1.1036(4)	0.055(1)
C(04)	0.3330(3)	0.8421(4)	1.0634(4)	0.056(1)
O(04)	0.3546(3)	0.9395(3)	1.1321(4)	0.081(1)
C(05)	0.3932(3)	0.8280(4)	0.9494(4)	0.057(1)
C(06)	0.3721(3)	0.7353(3)	0.8713(4)	0.051(1)
C(1)	0.2277(8)	1.0198(7)	0.4538(8)	0.149(4)
C(2)	0.3290(8)	0.9705(7)	0.4881(7)	0.150(4)
O(1)	0.2017(3)	0.9984(3)	0.3295(4)	0.096(2)
C(1′)	0.1059(5)	1.0545(6)	0.2915(8)	0.117(3)
C(2′)	0.0840(5)	1.0393(7)	0.1547(8)	0.129(3)

residue is a four electron donor; formal electron counting reveals that **1** has 48 e, electron precise for a triangular cluster.

Cluster **1** has the same core structure as $Os_3(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}N,C\text{-}PhN{=}CMeC^iPr](CO)_9$ (**2**), which was obtained in 28% yield from the above-mentioned reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with $PhN{=}CMeCH{=}CMe_2$ [10], although the structure of **2** was defined less accurately. The crystallographic locations of the hydrides in **1** are consistent with the indirectly assigned hydrido ligand locations in **2**. The M(1)–N(01) distances [2.134(3) Å **1**, 2.139(9) Å **2**] are comparable, but the M(2)–C(012) [2.150(3) **1**, 2.201(10) Å **2**] and M(3)–C(012) [2.135(3) Å **1**, 2.256(10) Å **2**] interactions are shorter and the bridge more symmetric for **1**. The C(011)–C(012) distances [1.451(5) Å **1**, 1.400(14) Å **2**] are not significantly different, being within 3σ of each other; for **2**, this "short" C–C distance was ascribed to partial multiple bonding between the iminyl and carbenoid carbons, but the better-defined distance in **1** does not support the presence of partial multiple-bond character in this structural type.

2.3. Dynamic NMR behaviour of 1

The broadening observed with some ^{13}C NMR resonances of **1** at room temperature prompted us to examine its dynamic NMR behaviour. Fig. 2 presents stack plots showing the temperature evolution of the significant resonances. The low temperature limiting spectrum of the carbonyl region contains nine resonances, consistent with the solid state structure. Except for the signal at 197.9 ppm, all carbonyl resonances undergo broadening and coalescence between 265 K and the highest temperature recorded (323 K). The aromatic CH signals undergo pairwise coalescence at 260 K (121.6 ppm) and 240 K (116.1 ppm), corresponding to a value of $\Delta G^{\neq}$ of 49.2 ± 0.6 kJ mol^{-1}. There are two possible explanations for the observed dynamic NMR behaviour of the aryl resonances: restricted rotation about the aryl C–N linkage, or hydride hopping between Ru(1)–Ru(2) and Ru(1)–Ru(3); our results thus far do not permit us to distinguish between them. The rotational barrier for the former would be enhanced by the electron-donating hydroxy group; in related work, the isomerization about the C=N linkage of *p*-substituted hexafluoroacetone *N*-phenylimines was found to be facilitated by electron-donating substituents, with the resonance contribution involving an N–C(aryl) double bond becoming more important with increasing the donor strength of the substituent [11].

2.4. Synthesis and characterization of 3

It was of interest to investigate an analogous reaction with the asymmetric ketimine 4-hydroxyphenyl-*N*,*N*-isobutylmethylimide; in principle, two products from a double C–H activation are possible (Fig. 3). The reaction of $Ru_3(CO)_{12}$ with this imine afforded $Ru_3(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}(N,C)\text{-}4\text{-}HOC_6H_4N{=}C^iBuCH](CO)_9$ (**3**), in which double oxidative addition of imine-bound methyl has occured specifically. The spectra of the product cluster are similar to those of **1**, with the important difference of the presence of the readily-iden-

Table 3
Important bond lengths (Å) and angles (°) for **1**

Ru(1)–Ru(2)	2.985(1)	Ru(1)–Ru(3)	2.7823(8)
Ru(2)–Ru(3)	2.8002(8)	Ru(1)–N(01)	2.134(3)
Ru(2)–C(012)	2.150(3)	Ru(3)–C(012)	2.135(3)
N(01)–C(011)	1.301(4)	C(011)–C(012)	1.451(5)
C(011)–C(013)	1.497(6)	N(01)–C(01)	1.448(4)
C(01)–C(02)	1.387(5)	C(02)–C(03)	1.382(6)
C(03)–C(04)	1.379(5)	C(04)–C(05)	1.369(6)
C(05)–C(06)	1.386(6)	C(06)–C(01)	1.379(5)
Ru(1)–C(11)	1.906(4)	Ru(1)–C(12)	1.947(4)
Ru(1)–C(13)	1.901(4)	Ru(2)–C(21)	1.901(4)
Ru(2)–C(22)	1.909(4)	Ru(2)–C(23)	1.954(4)
Ru(3)–C(31)	1.907(4)	Ru(3)–C(32)	1.893(4)
Ru(3)–C(33)	1.934(4)	Ru(1)–H(1)	1.77(5)
Ru(2)–H(1)	1.81(6)	Ru(2)–H(2)	1.65(3)
Ru(3)–H(2)	1.85(4)		
Ru(1)–Ru(2)–Ru(3)	57.39(2)	Ru(2)–Ru(3)–Ru(1)	64.64(2)
Ru(3)–Ru(1)–Ru(2)	57.97(2)	Ru(2)–Ru(1)–N(01)	83.21(7)
Ru(3)–Ru(1)–N(01)	84.83(8)	Ru(1)–Ru(2)–C(012)	70.70(9)
Ru(3)–Ru(2)–C(012)	48.96(9)	Ru(1)–Ru(3)–C(012)	75.33(9)
Ru(2)–Ru(3)–C(012)	49.43(9)	Ru(1)–N(01)–C(011)	116.7(2)
Ru(1)–N(01)–C(01)	123.8(2)	Ru(2)–C(012)–C(011)	117.3(2)
Ru(3)–C(012)–C(011)	118.4(2)	C(012)–C(011)–C(013)	118.0(3)
C(012)–C(011)–N(01)	119.7(3)	C(013)–C(011)–N(01)	122.3(3)

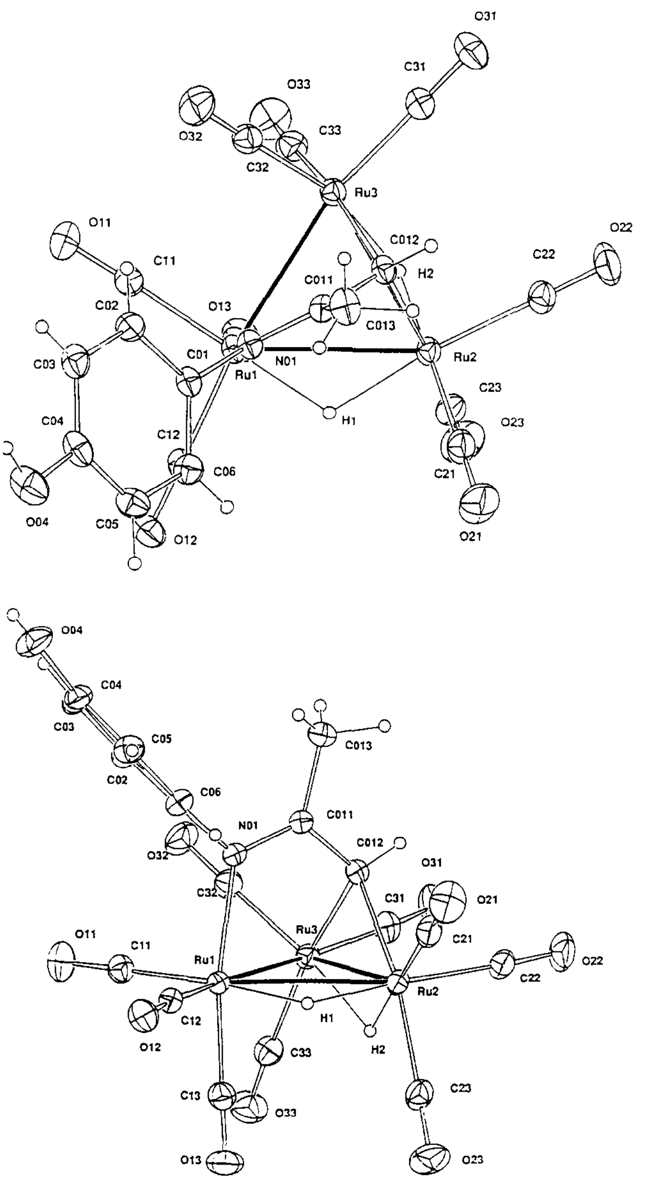

Fig. 1. Molecular structure and atomic labelling scheme for $Ru_3(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}(N,C)\text{-}4\text{-}HOC_6H_4N{=}CMeCH](CO)_9 \cdot Et_2O$ (**1**). 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å. Projections are shown normal and oblique to the Ru_3 plane.

tified spectral signatures of the isobutyl group. This reaction type is thus specific for methyl groups adjacent to the imine function for the examples investigated.

3. Experimental details

The carbonyl $Ru_3(CO)_{12}$ was synthesized by a published procedure [12]. 4-Aminophenol (Fluka) and 4-methyl-2-pentanone (Aldrich) were used as received. Cyclohexane (sodium) and acetone (calcium sulfate) were dried and distilled before use. The reactions were carried out using Schlenk techniques [13] under nitrogen, although subsequent work-up was carried out without any precautions to exclude air. Thin layer chromatography (TLC) was on glass plates (20 × 20 cm) coated with Merck GF_{254} silica gel (0.5 mm). For

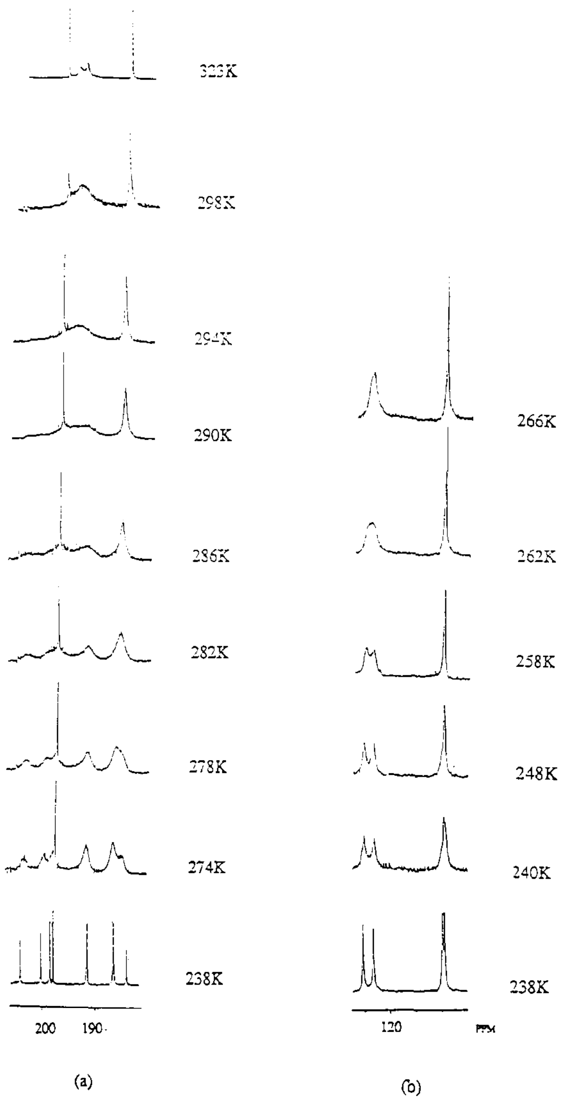

Fig. 2. Variable temperature ^{13}C NMR spectra for **1**; (a) metal-bound carbonyl region; (b) *o*- and *m*-carbons of the 4-hydroxyphenyl group.

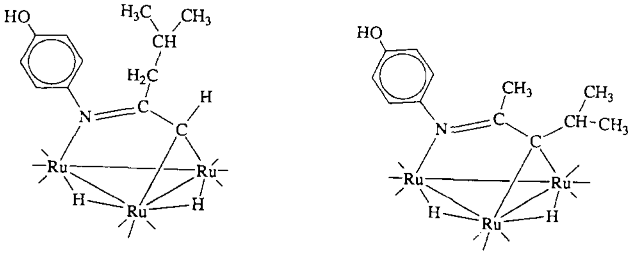

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Fig. 3.

column chromatography Kieselgel 60 (70–230 mesh ASTM) was used.

The IR spectra were recorded with a Perkin-Elmer model 1725 Fourier-transform spectrophotometer with CaF_2 optics. The NMR spectra were recorded on a Bruker AM300 spectrometer, the ^1H spectra at 300.13 MHz and the ^{13}C spectra at 75.47 MHz with approximately 0.02 M $Cr(acac)_3$ as the relaxation agent and a recycle delay of 0.5 s. The FAB mass spectra were recorded with a VG ZAB 2HF instrument (exciting gas Ar, source pressure 10^{-6} mbar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix) at the University of Adelaide. Elemental microanalyses were performed by the Microanalysis Service Unit in the Department of Chemistry, University of Queensland. Decomposition temperatures and melting points were measured in sealed capillaries with a Gallenkamp melting point apparatus.

3.1. Preparation of 4-hydroxyphenyl-N,N-dimethylimide

A mixture of 4-aminophenol (2.4 g, 0.022 mol) and acetone (50 ml) was warmed to give a pale purple solution, which was stirred for 30 min. The solution was cooled to 4 °C, and the pink to off-white crystals formed were collected and washed with acetone. The product was dried briefly *in vacuo* before being sublimed under vacuum (160–180 °C, 0.1 Torr) to give pale-yellow crystals of 4-hydroxyphenyl-*N*,*N*-dimethylimide (1.8 g, 0.012 mol, 55%). MP 165 °C. Anal. Found: C, 72.04; H, 7.51; N, 9.45%; *m/z* M^+ 149. $C_9H_{11}NO$ Calc.: C, 72.45; H, 7.43; N, 9.39%; M^+ 149. IR (Nujol): 1657s (C=N) cm^{-1}. ^1H NMR: $\delta(d_6$-acetone) 8.07 (s, 1H, OH); 6.76 (d, *J*(HH) = 9 Hz (2H), C_6H_4); 6.52 (d, *J*(HH) = 9 Hz (2H), C_6H_4); 2.89 (s, 3H, Me), 1.79 (s, 3H, Me). ^{13}C NMR: $\delta(d_6$-DMSO) 168.0 (C=N); 153.1 (COH); 142.9 (aryl CN); 120.6, 115.4 (aryl CH); 28.1, 20.1 (Me).

3.2. Preparation of 4-hydroxyphenyl-N,N-isobutylmethylimide

4-Aminophenol (2.5 g, 0.023 mol) was dissolved in 4-methyl-2-pentanone (60 ml) and the solution heated under reflux for 24 h as water was removed with a Dean-Stark trap. The product was collected and recrystallized from methanol to afford tan crystals of 4-hydroxyphenyl-*N*,*N*-isobutylmethylimide (3.7 g, 0.019 mol, 83%). MP: 151–154 °C. Anal. Found: C, 74.99; H, 9.28; N, 7.05%; *m/z* M^+ 191. $C_{12}H_{17}NO$ Calc.: C, 75.35; H, 8.96; N, 7.32%; M^+ 191. IR (Nujol): 1665s (C=N). ^1H NMR: $\delta(d_6$-DMSO) 9.02 (s, 1H, OH); 6.68 (d, *J*(HH) = 9 Hz (2H), C_6H_4); 6.45 (d, *J*(HH) = 9 Hz (2H), C_6H_4); 2.18 (d, *J*(HH) = 6 Hz (2H), CH_2–CH); 2.09 (m, 1H, CH_2–$CHMe_2$); 1.70 (s, 3H, Me); 0.92 (d, *J*(HH) = 6 Hz, CH*Me*). ^{13}C NMR: $\delta(d_6$-DMSO) 170.2 (C=N); 153.0 (COH); 143.0 (aryl CN); 120.4, 119.4 (aryl CH); 49.9 (CH_2); 25.4 (CH); 22.4 (CH*Me*); 19.3 (=C*Me*).

3.3. Reaction of $Ru_3(CO)_{12}$ with 4-hydroxyphenyl-N,N-dimethylimide

A mixture of $Ru_3(CO)_{12}$ (120 mg, 0.188 mmol) and 4-hydroxyphenyl-*N*,*N*-dimethylimide (200 mg, 1.9 mmol) in cyclohexane (20 ml) was refluxed for 22 h at which stage a yellow-brown precipitate was evident in the dark reaction mixture. The solvent was removed *in vacuo*, the residue taken up in dichloromethane (20 ml), and the solution filtered to remove some of the residual Schiff base. Thin layer chromatography with 50% acetone in light petroleum (b.p. 40–70 °C) as eluent afforded a trace amount of unchanged $Ru_3(CO)_{12}$ and a major yellow band (R_f 0.5) from which a powder was isolated from hexane at −20 °C and identified as $Ru_3(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}(N,C)\text{-}4\text{-}HOC_6H_4N{=}CMe\text{-}CH](CO)_9$ (**1**; 110 mg, 0.15 mmol, 81%). Anal. Found: C, 30.71; H, 1.49; N, 2.14%; $[M-CO]^+$ 678. $C_{18}H_{11}NO_{10}Ru_3$ Calc: C, 30.69; H, 1.57; N, 1.99%; *m/z* M^+ 706. IR (cyclohexane): ν(CO) 2098s, 2070vs, 2046vs, 2023s, 2020s, 2005s, 2001s, 1986m, 1978m cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 6.79 (d, *J*(HH) = 9 Hz (2H), C_6H_4); 6.51 (d, *J*(HH) = 9 Hz (2H), C_6H_4); 4.84 (s, 1H, OH); 4.65 (s, 1H, CH); 1.68 (s, 3H, Me); −12.34 (d, *J*(HH) = 3 Hz (1H), RuH); −14.82 (d, *J*(HH) = 3 Hz (1H), RuH). ^{13}C NMR at 298 K: $\delta(CDCl_3)$ 212.1 (C=N); 197.9, 195.2 (br), 185.6 (CO); 152.9 (COH); 147.6 (aryl CN); 121.6, 116.1 (aryl CH); 81.0 (CH); 24.9 (Me). ^{13}C NMR at 238 K: $\delta(CDCl_3)$ 211.9 (N=C); 204.2, 200.4, 198.6, 197.9, 191.6, 191.4, 186.7, 186.5, 184.3 (CO); 152.3 (COH); 147.2 (aryl CN); 122.1, 121.3, 116.0, 115.8 (aryl CH); 80.5 (RuCH); 24.9 (Me).

3.4. Reaction of $Ru_3(CO)_{12}$ with 4-hydroxyphenyl-N,N-isobutylmethylimide

A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and 4-hydroxyphenyl-*N*,*N*-isobutylmethylimide (200 mg, 1.1 mmol) in cyclohexane (50 ml) was refluxed for 24 h. The mixture was reduced to dryness, and the residue taken up in a minimum of dichloromethane and placed on a small amount of silica. Column chromatography with light petroleum (b.p. 40–70 °C) as eluent afforded trace amounts of unchanged starting material and $Ru_4(\mu\text{–}H)_4(CO)_{12}$. Elution with diethyl ether gave the major product, which was isolated as a yellow oil from dichloromethane/hexane and identified as $Ru_3(\mu\text{-}H)_2[\mu_3\text{-}\eta^2\text{-}(N,C)\text{-}4\text{-}HOC_6H_4N{=}C^iBuCH]$ $(CO)_9$ (**3**; 125 mg, 54%). FAB MS Found: M^+ 748. $C_{21}H_{17}NO_{10}Ru_3$ Calc.: *m/z* M^+ 748. IR (cyclohexane): ν(CO) 2097m, 2071s, 2045s, 2029m, 2019m, 2005sh, 2001s, 1986m, 1977m br cm^{-1}. ^1H NMR: δ ($CDCl_3$) 6.77 (d, J(HH) = 8 Hz (2H), C_6H_4); 6.49 (d, J(HH) = 8 Hz (2H), C_6H_4); 5.18 (s, 1H, OH); 4.79 (s, 1H, RuCH); 1.92–1.85 (m, 3H, $CH_2 + CH_2CH$); 0.78 (d, J(HH) = 6 Hz (6H), Me); −12.39 (d, J(HH) = 3 Hz (1H), RuH); −14.79 (d, J(HH) = 3 Hz (1H), RuH). ^{13}C NMR: δ ($CDCl_3$) 214.8 (C=N); 206.9, 206.3, 205.6, 197.9, 196.1, 185.7 (CO); 153.1 (aryl CN); 147.0 (COH); 122.5, 115.9 (aryl CH); 80.2 (RuCH); 46.6 (CH_2); 27.7 (CH_2CH); 23.2 ($CH\text{-}CH_3$). The compound retained traces of solvent tenaciously; all attempts to isolate it as a solid rather than as a yellow oil were unsuccessful. However, all spectra obtained for **3** are consistent with the presence of a single organometallic product.

3.5. Structure determination

Single crystals of compound **1** suitable for diffraction analyses were grown from a dichloromethane/diethyl ether solution at −30 °C. A unique diffractometer data set was measured at ~ 295 K within the specified $2\theta_{max}$ limit ($2\theta/\theta$ scan mode; monochromatic Mo K_α radiation ($\lambda = 0.7107_3$ Å)) yielding N independent reflections. N_0 of these with $I > 3\sigma(I)$ were considered 'observed' and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were refined for the main molecule and constrained at estimated values for the solvent. Conventional residuals R, R_w on $|F|$ at convergence are given, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4\ (I_{diff})$ being used. Neutral atom complex scattering factors were used, computation using the XTAL 3.2 program system [14] implemented by S.R. Hall. Pertinent results are given in the figure and Tables. Tables of atomic coordinates and thermal parameters and a complete list of bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Rd, Cambridge, CB2 1E2, UK.

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