Concurrent Rearrangement of Phenylimido and Alkenyl Ligands on a WRu_2 Metal Triangle†

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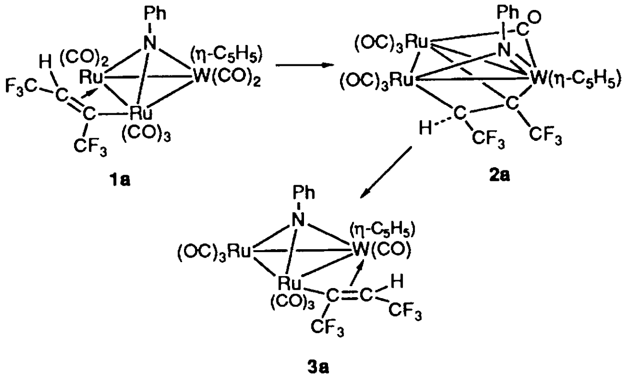
Thermolysis of the phenylimido cluster $[WRu_2(\eta\text{-}C_5Me_5)(CO)_7(\mu_3\text{-}NPh)(CF_3CCHCF_3)]$ **1b** in refluxing toluene yielded a hydrido–alkyne complex $[WRu_2(\eta\text{-}C_5Me_5)(CO)_6H(\mu\text{-}NPh)\{C_2(CF_3)_2\}]$ **4** *via* CO elimination and alkenyl C–H activation. Treatment of **4** with CO in refluxing toluene induced the formation of a second alkenyl complex $[WRu_2(\eta\text{-}C_5Me_5)(CO)_7(\mu\text{-}NPh)(CF_3CCHCF_3)]$ **2b** containing a doubly bridging imido ligand and face-bridging alkenyl ligand. This transformation between **4** and **2b** is reversible since complex **4** can be regenerated by thermolysis of **2b** in toluene. Complexes **4** and **2b** were also examined by single-crystal X-ray diffraction. Crystal data for **4**: triclinic space group $P\bar{1}$; $a = 10.332(1)$, $b = 17.296(4)$, $c = 18.351(2)$ Å, $\alpha = 110.81(1)$, $\beta = 106.31(1)$, $\gamma = 92.46(2)°$, $Z = 4$; final $R = 0.026$, $R' = 0.024$ for 6445 reflections with $I > 2\sigma(I)$. Crystal data for **2b**: monoclinic, space group $P2_1/n$; $a = 11.398(3)$, $b = 22.965(6)$, $c = 11.670(3)$ Å, $\beta = 99.78(2)°$, $Z = 4$; final $R = 0.025$, $R' = 0.024$ for 3526 reflections with $I > 2\sigma(I)$.

The chemistry of transition-metal complexes possessing nitrogen-donor[1] and imido ligands[2] has been investigated extensively. In this area, we have been interested in the synthesis of polynuclear imido clusters *via* treatment of the triruthenium phenylimido cluster $[Ru_3(CO)_{10}(\mu_3\text{-}NPh)]$ with tungsten acetylide and hydride complexes.[3] The heterometallic clusters $[WRu_2(L)(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)]$ ($L = C_5H_5$ or C_5Me_5), containing a triply bridging imido ligand, have been prepared by the respective reaction with $[WL(CO)_3H]$.[3b] In contrast to the reactions of $[Ru_3(CO)_{10}(\mu_3\text{-}NPh)]$ with alkyne molecules, which afforded a metallapyrrolidone complex as the major product *via* cluster fragmentation,[4] the reaction of WRu_2 imido complexes with hexafluorobut-2-yne affords alkenyl complexes $[WRu_2(L)(CO)_7(\mu_3\text{-}NPh)(CF_3CCHCF_3)]$ ($L = C_5H_5$ **1a** or C_5Me_5 **1b**) in high yield. Spectroscopic data indicate that their structures are identical; however, they exhibit very different behaviour in reactivity. Complex **1a** undergoes thermally induced concurrent migration of the alkenyl and imido ligands on the triangular Ru_2W core, affording two structural isomers (Scheme 1), but in the absence of CO complex **1a** decomposes rapidly to give no tractable cluster complex.[5] In contrast, the respective C_5Me_5 derivative **1b** is essentially inert under a CO atmosphere but reacts thermally by eliminating one CO molecule to afford the alkyne complex $[WRu_2(\eta\text{-}C_5Me_5)(CO)_6H(\mu\text{-}NPh)\{C_2(CF_3)_2\}]$ **4** when the CO atmosphere is removed. In this paper we report the full details of the reactions involving **1b** and delineate the cause of the difference between **1a** and **1b**.



Scheme 1

Experimental

General.—Infrared spectra were recorded on a Bomen M-100 FT-IR spectrometer. Proton, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AM-400 or Varian Unity-400 (400.13 MHz) instruments. Mass spectra were obtained on a JEOL-HX110 spectrometer operating in the fast atom bombardment (FAB) mode. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. The progress of the reactions was monitored by thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck) and the products were separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, E. Merck). The phenylimido complex $[WRu_2(\eta\text{-}C_5Me_5)(CO)_7(\mu_3\text{-}NPh)(CF_3CCHCF_3)]$ was prepared from the reaction of $[WRu_2(\eta\text{-}C_5Me_5)(CO)_8(\mu\text{-}H)(\mu_3\text{-}NPh)]$ with hexafluorobut-2-yne in toluene (105 °C, 10 min). Elemental analyses were performed at the NSC Regional Instrument Center at the National Cheng Kung University, Tainan, Taiwan.

Pyrolysis of $[WRu_2(\eta\text{-}C_5Me_5)(CO)_7(\mu_3\text{-}NPh)(CF_3CCHCF_3)]$.— A toluene solution ($40\ cm^3$) of $[WRu_2(\eta\text{-}C_5Me_5)(CO)_7(\mu_3\text{-}NPh)(CF_3CCHCF_3)]$ **1b** (100 mg, 0.103 mmol) was heated at reflux under nitrogen for 30 min. After evaporation of the solvent under vacuum the residue was separated by thin-layer chromatography (dichloromethane–hexane 1:2), giving 26 mg of dark brown $[WRu_2(\eta\text{-}C_5Me_5)(CO)_6H(\mu\text{-}NPh)\{C_2(CF_3)_2\}]$ **4** (0.028 mmol, 27%) and 28 mg of starting material (28%) in the order of elution. Complex **4** was further purified by recrystallization from dichloromethane–hexane at room temperature. Spectral data for **4**: MS (FAB, ^{102}Ru, ^{184}W),

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

Non-SI unit employed: atm ≈ 101 325 Pa.

Table 1 Experimental data for the X-ray diffraction studies

Compound	**4**	**2b**
Empirical formula	$C_{26}H_{21}F_6NO_6Ru_2W$	$C_{27}H_{21}F_6NO_7Ru_2W$
M	943.44	971.45
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a/Å	10.332(1)	11.398(3)
b/Å	17.296(4)	22.965(6)
c/Å	18.351(2)	11.670(3)
α/°	110.81(1)	
β/°	106.31(1)	99.78(2)
γ/°	92.46(2)	
U/Å^3	2904.7(9)	3010(1)
Crystal size/mm	0.20 × 0.30 × 0.50	0.35 × 0.40 × 0.55
D_c/g cm^{-3}	2.157	2.144
$F(000)$	1792	1848
Maximum 2θ/°	45	45
Range h,k,l	−11 to 11, 0–18, −19 to 18	−12 to 12, 0–24, 0–12
μ(Mo-Kα)/mm^{-1}	5.12	4.95
Maximum, minimum transmission factors	1.00, 0.67	1.00, 0.51
No. of unique data	7573	3918
Data with $I > 2\sigma(I)$	6445	3526
No. of parameters	758	398
R, R', S	0.026, 0.024, 2.63	0.025, 0.024, 2.87
Maximum Δ/σ ratio	0.039	0.031
Maximum, minimum residual electron density/e Å^{-3}	1.41, 0.94	0.61, −0.98

* Features common to both determinations: $Z = 4$, λ(Mo-Kα) = 0.709 30 Å, $T = 297$ K, $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$, $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$, $S = [\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{\frac{1}{2}}$, $w^{-1} = \sigma^2(F)$ (N_o = number of observations; N_v = number of variables).

m/z 945 (M^+); IR (C_6H_{12}) ν(CO) 2078vs, 2045vs, 2014s, 2008s, 1988m and 1980m cm^{-1}; NMR [CD_2Cl_2, room temperature (r.t.)]: ^{1}H, δ 7.26 [t, 2 H, J(H–H) 7.7], 7.13 [t, 1 H, J(H–H) 7.4], 6.89 [d, 2 H, J(H–H) 6.9], 1.98 (s, 15 H) and −5.83 [s, 1 H, J(W–H) 122 Hz]; ^{19}F, δ −46.13 [q, 3 F, J(F–F) 13.0] and −50.2 [br q, 3 F, J(F–F) 13.0 Hz]; ^{13}C, δ 202.9, 198.1, 196.1, 195.3, 194.0, 187.4 (CO), 163.2 [*ipso*-C_6H_5, J(C–W) 21], 134.4 [q, CF_3, J(C–F) 271 Hz], 133.9 [q, *C*CF_3, J(C–F) 40], 129.9 (*o*-, *m*-C_6H_5), 129.7 [q, *C*CF_3, J(C–F) 40], 127.4 [q, *C*F_3, J(C–F) 274 Hz], 126.3 (*p*-C_6H_5), 120.3 (br, *m*-, *o*-C_6H_5), 112.2 (*C*$_5$Me$_5$) and 11.8 (C$_5$*Me*$_5$) (Found: C, 33.00; H, 2.30; N, 1.45. Calc. for $C_{26}H_{21}F_6NO_6Ru_2W$: C, 33.10; H, 2.25; N, 1.50%).

Treatment of Complex **4** *with* CO.—A toluene solution (35 cm^3) of complex **4** (31 mg, 0.032 mmol) was heated at reflux under CO for 8 min, during which the colour changed gradually from dark- to light-brown. After the mixture was cooled to room temperature the solvent was removed *in vacuo* and the residue separated by thin-layer chromatography with hexane as eluent, giving 16 mg of amber [WRu$_2$(η-C$_5$Me$_5$)(CO)$_7$(μ-NPh)(CF$_3$CCHCF$_3$)] **2b** (0.0164 mmol, 51%) and a green unknown material which decomposed readily during TLC separation. Complex **2b** was further purified by recrystallization from dichloromethane–hexane at room temperature. Spectral data for **2b**: MS (FAB, ^{102}Ru, ^{184}W), m/z 973 (M^+); IR (C_6H_{12}): ν(CO) 2084vs, 2057vs, 2031vs, 2018w, 1997s, 1984w and 1738m cm^{-1}; NMR ($CDCl_3$, r.t.): ^{1}H, δ 7.31–7.23 (m, 2 H), 7.10 [t, 1 H, J(H–H) 6.4], 7.04 [dd, 1 H, J(H–H) 0.8, 7.8], 6.55 [dd, 1 H, J(H–H) 0.8, 7.8], 3.43 [q, 1 H, J(F–H) 11.2 Hz] and 1.95 (s, 15 H); ^{19}F, δ −48.99 [q, 3 F, J(F–F) 8.3] and −52.09 [m, 3 F, J(F–F) 8.3, J(F–H) 11.2 Hz]; ^{13}C, δ 289.2 [J(W–C) 73], 201.6, 200.5, 197.8, 193.4, 192.0, 187.4 (CO), 163.9 [*ipso*-C_6H_5, J(W–C) 20], 133.7 [q, CF_3, J(C–F) 278], 130.5 [q, CF_3, J(C–F) 275], 129.1, 128.6, 125.9, 120.6, 118.3, 114.2 (*C*$_5$Me$_5$), 19.5 [q, *C*HCF$_3$, J(C–F) 25 Hz] and 10.7 (C$_5$*Me*$_5$) (Found: C, 33.15; H, 2.25; N, 1.45. Calc. for $C_{27}H_{21}F_6NO_7Ru_2W$: C, 33.40; H, 2.20; N, 1.45%).

Thermolysis of Complex **2b**.—A toluene solution (20 cm^3) of **2b** (8 mg, 0.008 mmol) was heated at reflux for 10 min, during which the colour changed gradually from light- to dark-brown. After allowing the mixture to cool to room temperature the solvent was removed *in vacuo* and the residue separated by thin-layer chromatography with hexane as eluent, giving 4.3 mg of **4** (0.0045 mmol, 56%).

Reaction of Complex **2b** *with* CO.—A toluene solution (20 cm^3) of **2b** (10 mg, 0.08 mmol) was heated at reflux under 1 atm of CO for 6 h. After cooling the mixture to room temperature the solvent was removed *in vacuo* and the residue separated by thin-layer chromatography with hexane as eluent, giving 6.3 mg of starting material **2b** (0.0064 mmol, 63%).

X-Ray Crystallography.—Diffraction measurements were carried out on a Nonius CAD-4 diffractometer. Lattice parameters of complex **4** were determined from 25 randomly selected reflections with 2θ angles in the range 16.88–41.20°, whereas the corresponding cell dimensions of complex **2b** were determined from 25 reflections with 2θ angles in the range 21.50–25.80°. All reflections were corrected for Lorentz, polarization and absorption effects. All data reduction and refinements were performed using the NRCC-SDP-VAX packages. The structures were solved by direct methods and refined by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. Complex **4** crystallized in the triclinic space group $P\bar{1}$; the hydride was not located, but the hydrogen atoms on the organic ligands were placed in idealized positions and were included in the structure factor calculation. For complex **2b** the space group $P2_1/n$ was identified on the basis of systematic absences. The combined data collection and refinement parameters are given in Table 1. Atomic positional parameters for complex **4** are found in Table 2, and some selected bond lengths and angles are given in Table 4. The corresponding parameters for complex **2b** are given in Tables 3 and 5, respectively.

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

Results and Discussion

Thermolysis of [WRu$_2$(η-C$_5$Me$_5$)(CO)$_7$(μ$_3$-NPh)(CF$_3$CCH-

Table 2 Atomic coordinates for complex **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1A)	0.515 69(3)	0.543 909(18)	0.283 003(18)	W(1B)	−0.020 06(3)	−0.039 789(18)	0.219 909(19)
Ru(1A)	0.772 61(5)	0.597 58(4)	0.396 73(4)	Ru(1B)	−0.258 58(6)	−0.128 15(4)	0.099 34(4)
Ru(2A)	0.646 06(6)	0.433 51(4)	0.352 68(4)	Ru(2B)	−0.197 95(6)	0.043 78(4)	0.136 36(4)
N(1A)	0.577 7(5)	0.641 2(3)	0.373 1(3)	N(1B)	−0.043 1(5)	−0.141 4(4)	0.137 8(4)
C(1A)	0.871 8(7)	0.701 2(5)	0.406 4(5)	C(1B)	−0.320 4(7)	−0.240 1(5)	0.091 4(5)
C(2A)	0.786 6(7)	0.625 2(4)	0.511 9(5)	C(2B)	−0.262 0(7)	−0.154 7(4)	−0.015 1(5)
C(3A)	0.933 9(7)	0.550 0(4)	0.408 8(5)	C(3B)	−0.440 8(8)	−0.106 3(5)	0.076 8(5)
C(4A)	0.633 4(7)	0.453 2(5)	0.461 0(5)	C(4B)	−0.171 5(8)	0.029 4(5)	0.031 0(5)
C(5A)	0.805 5(8)	0.383 4(5)	0.369 5(5)	C(5B)	−0.376 4(9)	0.069 5(6)	0.112 2(6)
C(6A)	0.531 9(8)	0.327 8(5)	0.303 4(5)	C(6B)	−0.121 1(9)	0.161 2(5)	0.182 8(6)
C(7A)	0.662 6(7)	0.381 3(5)	0.173 3(5)	C(7B)	−0.240 4(8)	0.088 1(5)	0.307 7(5)
C(8A)	0.660 6(6)	0.452 1(4)	0.247 2(4)	C(8B)	−0.207 2(7)	0.024 2(4)	0.241 3(4)
C(9A)	0.710 9(6)	0.535 4(4)	0.263 7(4)	C(9B)	−0.218 5(7)	−0.061 1(4)	0.229 7(4)
C(10A)	0.779 6(7)	0.568 5(5)	0.217 4(5)	C(10B)	−0.268 4(7)	−0.106 4(5)	0.275 5(5)
C(11A)	0.560 1(6)	0.721 3(4)	0.424 2(4)	C(11B)	−0.001 4(6)	−0.218 2(4)	0.095 4(5)
C(12A)	0.511 9(7)	0.728 3(5)	0.488 6(5)	C(12B)	0.050 5(8)	−0.223 0(5)	0.032 7(5)
C(13A)	0.491 4(8)	0.805 1(5)	0.537 8(5)	C(13B)	0.088 9(9)	−0.298 0(6)	−0.009 4(6)
C(14A)	0.519 7(8)	0.875 5(5)	0.522 7(5)	C(14B)	0.072 8(10)	−0.366 5(6)	0.011 6(7)
C(15A)	0.571 4(8)	0.869 3(5)	0.458 7(5)	C(15B)	0.023 2(9)	−0.360 7(5)	0.072 9(7)
C(16A)	0.592 0(7)	0.792 2(4)	0.409 6(5)	C(16B)	−0.016 5(8)	−0.287 2(5)	0.115 6(5)
C(17A)	0.278 6(6)	0.494 8(4)	0.233 0(5)	C(17B)	0.195 6(7)	0.044 7(5)	0.276 3(4)
C(18A)	0.330 2(6)	0.461 4(4)	0.166 4(4)	C(18B)	0.130 9(7)	0.067 6(4)	0.337 8(4)
C(19A)	0.381 7(6)	0.527 7(4)	0.148 9(4)	C(19B)	0.112 2(6)	−0.002 4(5)	0.358 3(4)
C(20A)	0.361 5(6)	0.603 3(4)	0.205 6(4)	C(20B)	0.164 6(7)	−0.067 2(5)	0.310 3(5)
C(21A)	0.296 7(6)	0.583 1(4)	0.256 3(4)	C(21B)	0.217 8(7)	−0.038 5(5)	0.259 8(5)
C(22A)	0.200 5(7)	0.445 3(5)	0.263 4(5)	C(22B)	0.249 3(8)	0.102 8(6)	0.243 1(6)
C(23A)	0.308 4(7)	0.369 2(5)	0.114 8(5)	C(23B)	0.113 1(8)	0.155 1(5)	0.382 3(6)
C(24A)	0.419 0(7)	0.520 2(5)	0.074 1(5)	C(24B)	0.071 0(8)	−0.003 0(6)	0.429 7(5)
C(25A)	0.391 7(8)	0.687 6(5)	0.203 7(5)	C(25B)	0.176 1(8)	−0.150 4(5)	0.318 1(6)
C(26A)	0.241 9(7)	0.641 8(5)	0.318 4(5)	C(26B)	0.295 8(8)	−0.082 8(6)	0.206 1(6)
O(1A)	0.938 6(6)	0.759 3(4)	0.415 6(4)	O(1B)	−0.367 2(6)	−0.303 6(4)	0.083 2(4)
O(2A)	0.791 5(5)	0.640 5(3)	0.577 5(3)	O(2B)	−0.260 0(6)	−0.169 3(3)	−0.078 1(3)
O(3A)	1.036 2(5)	0.526 3(4)	0.418 2(4)	O(3B)	−0.553 5(5)	−0.101 5(4)	0.061 1(4)
O(4A)	0.631 1(6)	0.464 0(4)	0.525 2(3)	O(4B)	−0.155 0(6)	0.021 9(4)	−0.028 8(4)
O(5A)	0.896 7(6)	0.350 5(4)	0.378 8(4)	O(5B)	−0.483 9(6)	0.086 4(5)	0.102 2(5)
O(6A)	0.461 1(7)	0.265 2(4)	0.275 8(5)	O(6B)	−0.066 5(8)	0.227 6(4)	0.207 5(5)
F(1A)	0.792 2(5)	0.371 8(3)	0.175 6(3)	F(1B)	−0.372 5(5)	0.074 0(3)	0.299 4(3)
F(2A)	0.605 1(5)	0.306 6(3)	0.165 9(3)	F(2B)	−0.214 9(5)	0.167 0(3)	0.312 7(3)
F(3A)	0.603 5(5)	0.385 8(3)	0.100 4(3)	F(3B)	−0.174 9(5)	0.094 1(3)	0.385 6(3)
F(4A)	0.913 4(4)	0.565 0(4)	0.240 6(3)	F(4B)	−0.403 0(4)	−0.131 9(3)	0.243 5(3)
F(5A)	0.771 4(5)	0.647 7(3)	0.231 2(3)	F(5B)	−0.213 4(5)	−0.174 1(3)	0.273 6(3)
F(6A)	0.737 1(5)	0.528 6(3)	0.136 0(3)	F(6B)	−0.248 1(5)	−0.060 7(3)	0.355 2(3)

Table 3 Atomic coordinates for complex **2b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.785 964(25)	0.912 799(11)	0.200 306(23)	C(19)	0.894 4(6)	0.995 3(3)	0.156 4(5)
Ru(1)	0.635 71(5)	0.885 520(23)	0.372 45(5)	C(20)	0.807 8(6)	0.983 5(3)	0.056 1(5)
Ru(2)	0.663 66(5)	0.808 571(23)	0.190 87(5)	C(21)	0.837 8(6)	0.928 9(3)	0.013 8(5)
N	0.721 3(5)	0.958 54(20)	0.298 9(4)	C(22)	0.942 0(6)	0.908 4(3)	0.082 5(6)
C(1)	0.638 7(6)	0.927 2(3)	0.516 9(6)	C(23)	1.086 7(6)	0.949 6(3)	0.261 7(7)
C(2)	0.477 8(6)	0.914 5(3)	0.301 3(6)	C(24)	0.909 4(7)	1.051 9(3)	0.222 7(7)
C(3)	0.564 9(7)	0.819 5(3)	0.422 6(7)	C(25)	0.713 2(7)	1.023 4(4)	−0.002 8(7)
C(4)	0.495 4(7)	0.797 6(3)	0.138 0(6)	C(26)	0.778 8(8)	0.903 4(4)	−0.101 4(6)
C(5)	0.681 7(7)	0.736 7(3)	0.285 7(7)	C(27)	1.019 5(8)	0.860 5(3)	0.051 5(8)
C(6)	0.709 2(6)	0.771 8(3)	0.058 3(6)	O(1)	0.636 9(5)	0.950 08(23)	0.602 8(4)
C(7)	0.627 2(6)	0.887 7(3)	0.098 5(6)	O(2)	0.385 4(4)	0.927 49(24)	0.264 2(5)
C(8)	0.939 5(6)	0.795 6(3)	0.293 2(6)	O(3)	0.520 5(6)	0.780 06(21)	0.457 6(5)
C(9)	0.836 6(6)	0.836 2(3)	0.296 9(5)	O(4)	0.395 8(5)	0.792 1(3)	0.109 1(5)
C(10)	0.809 2(6)	0.844 2(3)	0.419 5(5)	O(5)	0.689 9(6)	0.694 86(21)	0.335 7(5)
C(11)	0.897 0(6)	0.873 4(3)	0.507 4(6)	O(6)	0.734 6(5)	0.751 81(22)	−0.022 9(4)
C(12)	0.687 9(6)	1.016 8(3)	0.326 7(5)	O(7)	0.548 8(4)	0.905 64(21)	0.027 5(4)
C(13)	0.742 1(6)	1.044 1(3)	0.427 0(6)	F(1)	1.046 5(3)	0.820 61(16)	0.321 0(3)
C(14)	0.712 8(7)	1.100 9(3)	0.448 4(6)	F(2)	0.939 3(4)	0.770 95(16)	0.186 5(3)
C(15)	0.628 7(7)	1.129 9(3)	0.370 8(7)	F(3)	0.940 2(4)	0.749 06(16)	0.364 5(4)
C(16)	0.574 4(7)	1.102 8(3)	0.271 2(6)	F(4)	0.859 6(4)	0.879 88(21)	0.609 4(3)
C(17)	0.601 9(6)	1.046 1(3)	0.248 9(6)	F(5)	0.930 2(4)	0.927 13(16)	0.478 7(3)
C(18)	0.974 2(6)	0.948 1(3)	0.174 2(6)	F(6)	1.000 9(4)	0.844 79(18)	0.534 9(4)

Table 4 Selected bond distances (Å) and angles (°) for complex **4** with estimated standard deviations (e.s.d.s) in parentheses

	Molecule A	Molecule B
W(1)–Ru(1)	2.7504(8)	2.7416(9)
W(1)–Ru(2)	2.8432(8)	2.8352(8)
Ru(1)–Ru(2)	2.806(1)	2.804(1)
W(1)–N(1)	1.820(5)	1.816(6)
Ru(1)–N(1)	2.165(5)	2.188(5)
W(1)–C(8)	2.282(7)	2.328(6)
Ru(2)–C(8)	2.114(7)	2.097(7)
W(1)–C(9)	2.146(6)	2.136(6)
Ru(1)–C(9)	2.173(7)	2.161(7)
C(8)–C(9)	1.406(9)	1.408(10)
C(8)–C(7)	1.476(10)	1.461(10)
C(9)–C(10)	1.484(10)	1.504(10)
Ru–CO (mean)	1.920(8)	1.934(8)
W(1)–N(1)–Ru(1)	86.8(2)	85.9(2)
Ru–C–O (mean)	176.7(7)	175.7(7)

Table 5 Selected bond distances (Å) and angles (°) for complex **2b** with e.s.d.s in parentheses

W–Ru(1)	2.9206(9)	W–Ru(2)	2.7626(8)
Ru(1)–Ru(2)	2.8184(9)	W–N	1.805(5)
Ru(1)–N	2.187(5)	W–C(7)	2.070(6)
Ru(2)–C(7)	2.118(7)	W–C(9)	2.116(6)
Ru(2)–C(9)	2.234(6)	Ru(1)–C(10)	2.178(6)
C(8)–C(9)	1.506(9)	C(9)–C(10)	1.525(9)
C(10)–C(11)	1.468(9)	Ru–CO (mean)	1.929(7)
W–N–Ru(1)	93.5(2)	W–C(7)–O(7)	141.9(5)
Ru(2)–C(7)–O(7)	135.5(5)	Ru–C–O (mean)	177.0(7)

CF_3)] **1b** in toluene solution and under a nitrogen atmosphere for 30 min afforded a mixture of dark brown [WRu_2(η-C_5Me_5)$(CO)_6$H(μ-NPh){$C_2(CF_3)_2$}] **4** and starting material **1b** in 27% and 28% yields, respectively. Extending the reaction time to 1 h failed to deplete the starting material but reduced the overall yield of **4**. Complex **4** was purified by TLC followed by recrystallization. The FAB mass spectrum shows a molecular ion peak indicating that this molecule is generated *via* CO elimination. The IR spectrum in solution shows six CO stretches in the region 2078–1980 cm^{-1}. The ^1H NMR spectrum exhibits a high-field hydride resonance at δ −5.83 [*J*(W–H) 122 Hz], in addition to the signals expected for the C_5Me_5 and phenylimido groups. The relative chemical shift and the large tungsten–hydride coupling constant strongly suggest that the hydrogen atom of the vinyl group in **1b** has now transformed into a terminal hydride[6] linked directly to the tungsten atom. The ^{13}C NMR spectrum confirmed that there are six CO ligands associated with the ruthenium atoms. In addition, we can deduce that the phenylimido ligand adopts an uncommon asymmetric doubly bridging mode because the *ipso*-carbon of the phenyl substituent at δ 163.2 shows the presence of tungsten–carbon coupling [*J*(C–W) 21 Hz]. The *J*(C–W) coupling is consistent with the observation that the phenylimido group is linked to the tungsten atom *via* a W=N double bond.[5] For comparison, the *ipso*-carbons of mononuclear tungsten phenylimido complexes give *J*(W–C) coupling constants in the range 23–31 Hz.[7]

In order to elucidate and confirm the molecular structure of complex **4**, a single-crystal X-ray structure determination was undertaken. Crystals suitable for diffraction were obtained from CH_2Cl_2–heptane at room temperature. The X-ray crystal structure determination indicates that the unit cell contains two crystallographically distinct, but structurally similar molecules. An ORTEP diagram of one molecule is shown in Fig. 1, and selected bond parameters are presented in Table 4. The metal framework consists of a WRu_2 triangular arrangement with distances W(1A)–Ru(1A) 2.7504(8), W(1A)–Ru(2A) 2.8432(8) and Ru(1A)–Ru(2A) 2.806(1) Å. Each ruthenium atom is coordinated by three linear CO ligands, whereas the tungsten atoms bears a C_5Me_5 ligand. The phenylimido ligand bridges the W(1A)–Ru(1A) edge with bond distances W(1A)–N(1A) 1.820(5) and Ru(1A)–N(1A) 2.165(5) Å. The short W–N distance indicates the presence of a W=N double-bond interaction. Consequently, the imido ligand is best described as having the novel W=N(Ph)→Ru bonding mode. The related, isoelectronic W=O→Os interaction is well documented in WOs_3 clusters.[8] The dihedral angle between the WRu_2 and WRuN planes is 161.5(2)°.

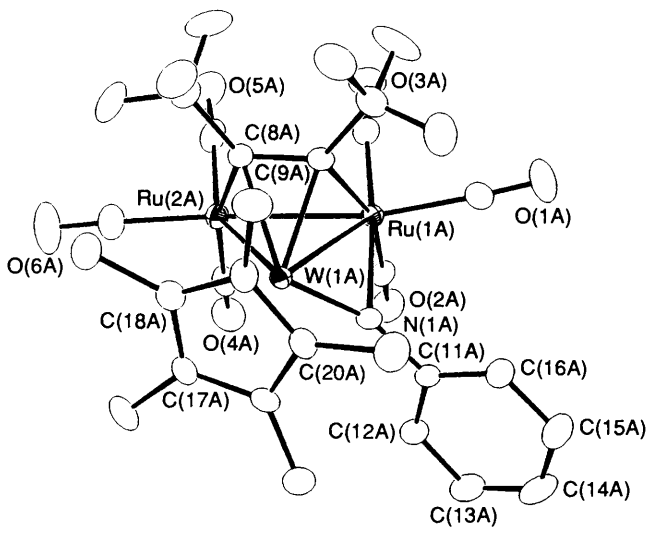


Fig. 1 Molecular structure of [WRu_2(η-C_5Me_5)$(CO)_6$H(μ-NPh){$C_2(CF_3)_2$}] **4** showing the atomic numbering scheme

On the opposite side of the phenylimido group is a coordinated hexafluorobut-2-yne molecule, which is produced from the alkenyl group, CCF_3=$CHCF_3$, of its precursor **1b**. This alkyne fragment adopts a typical 2σ + π bonding mode[9] with its C–C vector parallel to the unique Ru–Ru bond. The Ru–C distances are in the range 2.114(7)–2.173(7) Å while the W–C distances are slightly longer [2.146(6)–2.282(7) Å]. The ruthenium atoms constitute a pseudo-octahedral arrangement including the Ru–C interactions of the ligated alkyne; therefore, the hydride does not interact with these two ruthenium atoms but is bonded in a terminal mode to the tungsten atom. Consistent with this proposal, the tungsten atom shows a large unfilled space between the W(1A)–N(1A) and W(1A)–Ru(1A) bonds, near the C(4A)–O(4A) ligand of the Ru(2A) centre. This large opening is clearly caused by the presence of the terminal hydride ligand.

Complex **4** upon reaction with CO in refluxing toluene failed to regenerate **1b** but afforded instead a second alkenyl complex [WRu_2(η-C_5Me_5)$(CO)_7$(μ-NPh)(CF_3CCHCF_3)] **2b** in moderate yield. This reaction proceeded by addition of CO to a tungsten centre and insertion of a ligated alkyne fragment to the W–H bond. Complex **2b** has been characterized by spectroscopic methods and by an X-ray diffraction study, indicating that its structure is analogous to the previously identified C_5H_5 derivative **2a**. The spectral data are given in the Experimental section, the ORTEP diagram appears in Fig. 2 and the essential bond parameters are included in Table 5. The phenylimido ligand of this complex bridges the longest metal–metal bond with W–Ru(1) 2.9206(9), W–Ru(2) 2.7626(8), Ru(1)–Ru(2) 2.8184(9), W–N 1.805(5) and Ru(1)–N 2.187(5) Å. Other important structural features include the bridging CO ligand linked to the W–Ru(2) bond and the *cis*-alkenyl group which adopts an unusual μ_3-η^2 mode.[10] Thermolysis of **2b** under a dinitrogen atmosphere regenerated **4** in refluxing toluene. No

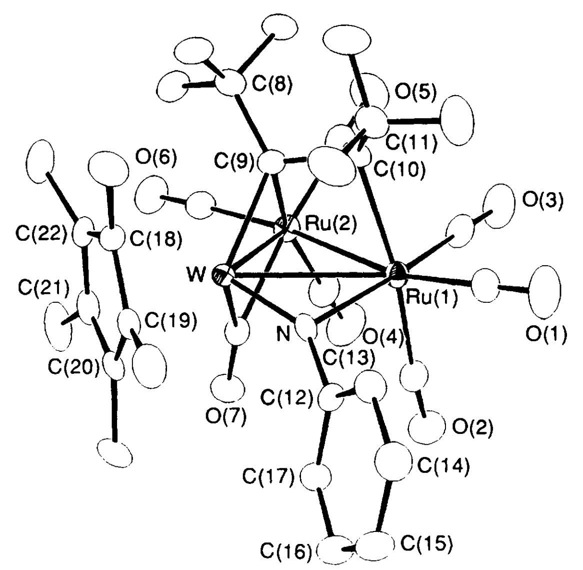
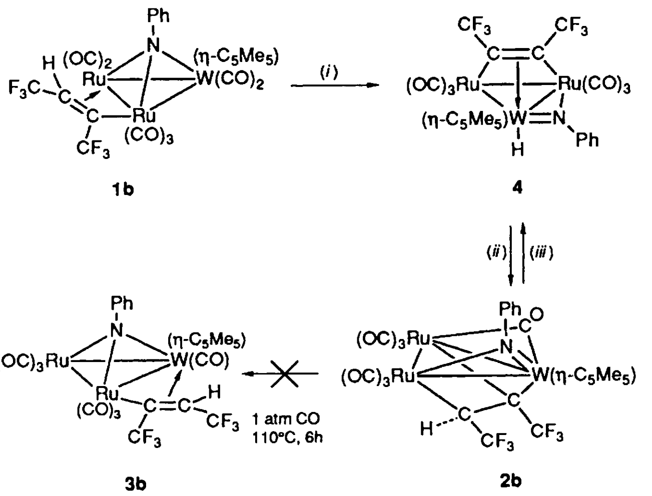


Fig. 2 Molecular structure of $[\mathrm{WRu_2(\eta\text{-}C_5Me_5)(CO)_7(\mu\text{-}NPh)(CF_3\text{-}CCHCF_3)}]$ **2b** showing the atomic numbering scheme



Scheme 2 (*i*) 110 °C, 30 min, **1b** (28%) and **4** (27%); (*ii*) 110 °C, 1 atm CO, 8 min (51%); (*iii*) 110 °C, 10 min (56%)

derivative **3b** (analogous to **3a**) was observed even upon extending the duration of the reaction to 1 h (Scheme 2).

The results described in this and an earlier communication[5] show that the imido ligands in these $\mathrm{WRu_2}$ clusters undergo facile μ_3 to μ interconversion and assist the alkenyl migration from μ, to μ_3 and back to μ modes. The formation of the stable W=N double bond contributes substantially to the stabilization of the μ-imido ligand, since the imido ligand of triruthenium cluster compounds invariably favours the μ_3 mode.[11] This dramatic change in reactivity and bonding is due to the presence of both the electropositive tungsten atom and ligated electron-donating η-$\mathrm{C_5H_5}$, η-$\mathrm{C_5Me_5}$ or pyrazolylborate ligands because these combinations tend to stabilize further multiple bonding to main-group, electronegative elements, such as oxygen and nitrogen.[12] In addition, many early-transition-metal complexes containing oxo ligands have been synthesized and reported recently.[13]

While thermolysis of **1a** under CO afforded **2a** as the kinetic product and **3a** as the thermodynamic product, the corresponding $\mathrm{C_5Me_5}$ derivative **1b** is stable and failed to produce any cluster compound under similar conditions. In the absence of CO gas, complex **1b** underwent CO elimination to afford **4** in low yield and, in turn, complex **4** reacted with CO to yield not **3b** but **2b** as the end product in moderate yield (Scheme 2). The transformation from **1b** to **2b** involves the intermediacy of complex **4**, indicating that the imido and alkenyl migration of the respective $\mathrm{C_5H_5}$ derivatives may also proceed *via* reversible CO elimination and formation of the hydrido–alkyne intermediate. Although this mechanism appears attractive, we disfavour this hypothesis on the basis of the following two observations: first, thermolysis of **1a** under an inert atmosphere leads to complete decomposition and secondly the yield of the product upon isomerization of **1a** or **2a** to **3a** is much greater than that of the formation of **4** from **2b**. Therefore, the transformation from **1a** to **2a**, which differs from the respective transformation from **1b** to **2b**, proceeds *via* a simultaneous μ_3- to μ-imido ligand migration and μ- to μ_3-alkenyl conversion. Furthermore, thermolysis of **2b** under CO for 6 h also failed to generate the desired derivative **3b** containing a μ_3-phenylimido ligand. We speculate that the inertness of **2b** may be due to the electron-releasing $\mathrm{C_5Me_5}$ ligand.[14] As the $\mathrm{C_5Me_5}$ ligand is a better electron-releasing group than $\mathrm{C_5H_5}$, its presence can further stabilize the W=N interaction and, therefore, retard the regeneration of the μ_3-imido mode and prohibit the formation of **3b**.

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