CLUSTER CHEMISTRY

XXXXVIII *. SOME REACTIONS OF $Ru_3(CO)_{12}$ WITH NITROGEN HETEROCYCLES. X-RAY CRYSTAL STRUCTURES OF $Ru_3(\mu\text{-}CO)_2(CO)_8(bipy)$ AND $Ru_3(\mu\text{-}H)\{\mu\text{-}N_2C_3H(CF_3)_2\text{-}3,5\}(CO)_{10}$

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(Received April 1st, 1986)

Summary

Reactions between $Ru_3(CO)_{12}$ and the nitrogen heterocycles pyridine, 2,2'-bipyridyl, pyrazole, 3,5-dimethylpyrazole and 3,5-bis(trifluoromethyl)pyrazole are described. Pyridine afforded the cyclometallated complex $Ru_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}$, which with excess pyridine formed $Ru_3(\mu\text{-}H)_2(\mu\text{-}NC_5H_4)_2(CO)_8$. 2,2'-Bipyridyl gave purple $Ru_3(\mu\text{-}CO)_2(CO)_8(bipy)$, shown by an X-ray structure to have an $Fe_3(CO)_{12}$-type structure, with the bipy chelating one of the CO-bridged Ru atoms. The pyrazoles gave $Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3HR_2)(CO)_{10}$ (R = H, Me or CF_3), in which the pyrazolide ligand spans an Ru–Ru bond also bridged by H, as shown by the X-ray structure of the CF_3 derivative. The bipyridyl and pyrazole complexes both crystallise in the monoclinic system, the former in space group $P2_1/n$ with unit cell dimensions a 7.834(2), b 25.818(2), c 11.717(1) Å, β 107.41(1)° with $Z = 4$ and the latter in space group $P2_1/c$, unit cell dimensions a 16.802(3), b 7.726(1), c 18.807(3) Å, β 114.24(1)° with $Z = 4$. The structures were refined by conventional least-squares methods with the use of 3336 (2993 for the pyrazole structure) reflections with $I > 2.5\sigma(I)$ to final $R = 0.031$ and $R_w = 0.034$ (0.025 and 0.026).

Introduction

Relatively few derivatives of $Ru_3(CO)_{12}$ containing oxygen- or nitrogen-donor ligands have been described. In most cases this is the result of harsh reaction conditions leading to break-up of the cluster, as found with Schiff bases [1],

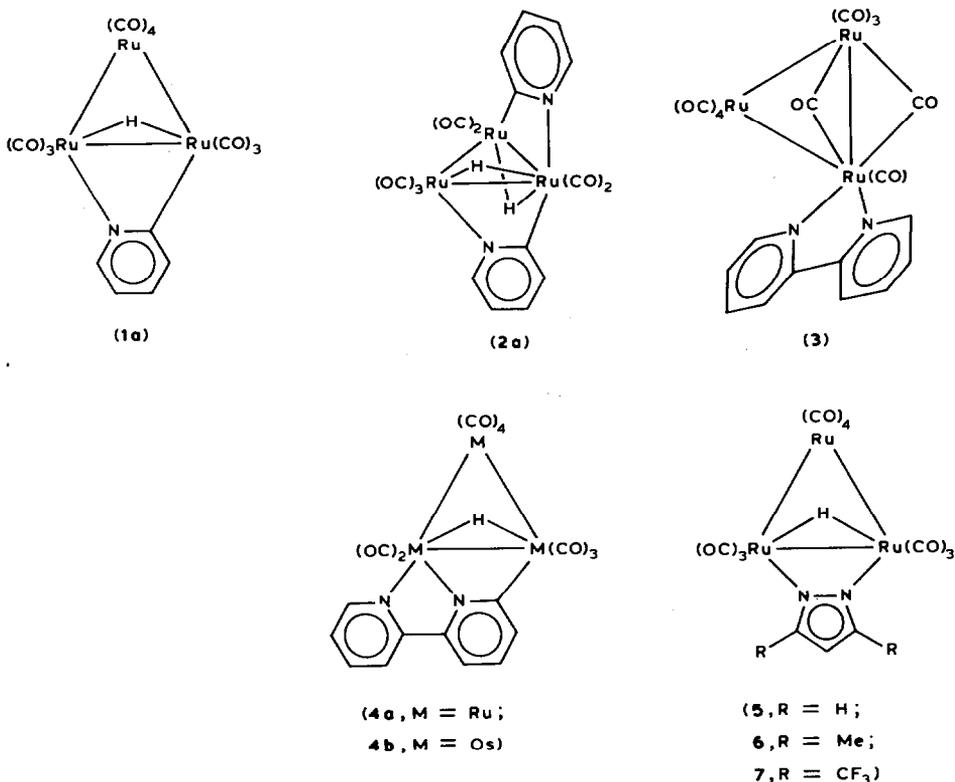---

* For Part XXXXVII, see ref. 20.

diazepines [2] or benzo[*h*]quinoline [3], for example. The dinitrogen heterocycle 1,2-diazine and some *cis*-diazenes, such as 2,3-diazanorbornene or 4-phenyl-3,3-bis(carbomethoxy)-1-pyrazoline, are exceptions, forming in good yield the carbonyl-bridged cluster $Ru_3(\mu\text{-}N_2C_4H_4)(\mu\text{-}CO)_2(CO)_8$ [4] or $Ru_3(\mu_3\text{-diazene})$-$(CO)_9$ [5], respectively. However, 8-quinolinol affords both an open Ru_3 cluster, $Ru_3(\mu_3\text{-}C_9H_6NO)_2(CO)_8$, in which one non-bonding edge of the Ru_3 cluster is spanned by two of the *N,O*-bonded heterocyclic ligands, and a mononuclear derivative [6]. This situation contrasts with the extensive derivative chemistry of $Os_3(CO)_{12}$, where both simple substitution and extensive cyclometallation reactions have been found [7]. We report herein some studies of the reactions between $Ru_3(CO)_{12}$ and some pyridine and pyrazole compounds, prompted by the recent accounts of related chemistry from Finland [8] and derived from the newly-reported $Ru_3(CO)_{10}(NCMe)_2$ [9]. Some of this work has been described in a preliminary fashion [10].

Results and discussion

Pyridine. The reaction between $Ru_3(CO)_{12}$ and pyridine was carried out in refluxing cyclohexane and gave in excellent yield a red-orange solid characterised as the cyclometallated complex $Ru_3(\mu\text{-}H)(\mu\text{-}NC_5H_4)(CO)_{10}$ (**1a**), analogous to similar complexes obtained from $Os_3(CO)_{12}$ [11,12]. Thus, the IR spectrum of **1a** contained a $\nu(CO)$ band pattern similar to that of the osmium analogue, while the ^1H NMR spectrum contained a resonance at δ -14.43 for the μ-H ligand. The resonances of the four protons of the C_5H_4N group appeared as three multiplets between δ 6.8 and 8.0 ppm, indicating the asymmetry of the ligand. Further heating with excess pyridine afforded a small amount of a second complex tentatively identified as $Ru_3(\mu\text{-}H)_2(\mu\text{-}NC_5H_4)_2(CO)_8$ (**2a**) by microanalysis and mass spectrometry only; the IR $\nu(CO)$ spectrum is similar to that found for the osmium analogue [11]. Compound **2a** has also been reported in the course of studies of complexes (mainly derived from $Os_3(CO)_{12}$) which might serve as models of the interactions of *N*-heterocycles with the active sites of heterogeneous hydrodenitrogenation catalysts; unfortunately, the $\nu(CO)$ spectrum was not recorded for this complex [13].

2,2′-Bipyridyl. Purple crystals of $Ru_3(\mu\text{-}CO)_2(CO)_8(bipy)$ (**3**) were similarly obtained in 92% yield from $Ru_3(CO)_{12}$ and 2,2′-bipyridyl. The IR spectrum contained a weak band at 1740 cm^{-1} in addition to three terminal $\nu(CO)$ bands suggesting that the complex is a rare example of an Ru_3 cluster with μ-CO ligands. This was confirmed by an X-ray study which is reported below. It is reported that a similar complex, formulated as containing the nitrogen heterocycle bridging one of the Ru–Ru bonds, undergoes ready cyclometallation to form $Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_{10}H_7)(CO)_9$ (**4a**) [9].

Pyrazoles. The reaction between $Ru_3(CO)_{12}$ and pyrazole was carried out in refluxing cyclohexane for 2 h and gave a mixture of products which was separable with considerable difficulty. Extensive thin layer chromatography and crystallisation eventually gave a mixture of $Ru_3(CO)_{12}$ and $Ru_4(\mu\text{-}H)_4(CO)_{12}$, together with some orange $Ru_3(\mu\text{-}H)(\mu\text{-}N_2C_3H_3)(CO)_{10}$ (**5**). This compound, which has formed by oxidative addition of the pyrazolide and H ligands to the cluster with concomitant loss of two CO groups, does not show any bands assignable to μ-CO groups in its IR spectrum. The metal-bonded proton resonates at δ -13.44 ppm, while the

(CO)₄
Ru

(CO)₃Ru———Ru(CO)₃

H

N

(1a)

(OC)₂Ru

(OC)₃Ru———Ru(CO)₂

H

H

N

N

(2a)

(CO)₃
Ru

(OC)₄Ru   OC   CO

Ru(CO)

N   N

(3)

(CO)₄
M

(OC)₂M———M(CO)₃

H

N   N

(4a, M = Ru;
4b, M = Os)

(CO)₄
Ru

(OC)₃Ru———Ru(CO)₃

H

N—N

R   R

(5, R = H;
6, R = Me;
7, R = CF₃)

symmetrical arrangement of the pyrazolide group is shown by the observation of the ring protons as two resonances at δ 6.26 and 7.50 ppm of relative intensities 1/2, respectively.

The 3,5-dimethyl analogue **6** was similarly obtained, being characterised by resonances in its ^{1}H NMR spectrum at δ 2.04 (Me), 5.72 (CH) and -13.23 ppm (RuH), with relative intensities 6/1/1. The corresponding 3,5-bis(trifluoromethyl) complex **7** was obtained in much higher yield (82%). All three complexes have similar IR ν(CO) spectra, and the ^{1}H NMR spectrum of **7** contained the two expected resonances at δ 6.78 (CH) and -13.16 ppm (RuH). The mass spectra of all complexes contain molecular ions which fragment by successive loss of the ten CO groups; complex **6** gave particularly strong doubly-charged ions corresponding to the singly-charged ions.

Molecular structure of Ru₃(μ-CO)₂(CO)₈(bipy)

A molecule of **3** is shown in Fig. 1. The three ruthenium atoms are joined by one short (2.757(1) Å) and two long (2.836(1), 2.855(1) Å) bonds. The two carbonyls C(1)–O(1) and C(2)–O(2) asymmetrically bridge the shortest Ru–Ru bond (Ru(1)–C(1) 1.963(5), Ru(3)–C(1), 2.217(6); Ru(1)–C(2), 2.029(6), Ru(3)–C(2), 2.089(5) Å); the shorter metal–carbon bond distances are formed by the Ru atom chelated by the bipyridyl ligand as a result of the higher electron density at this metal atom and increased back-bonding to the CO ligand. The asymmetry is also reflected in the Ru–C–O angles (144.7(5), 133.0(4)° at C(1) and 139.6(5), 136.3(4)° at C(2)). Of interest is the disparate asymmetry displayed by the bridging carbonyl
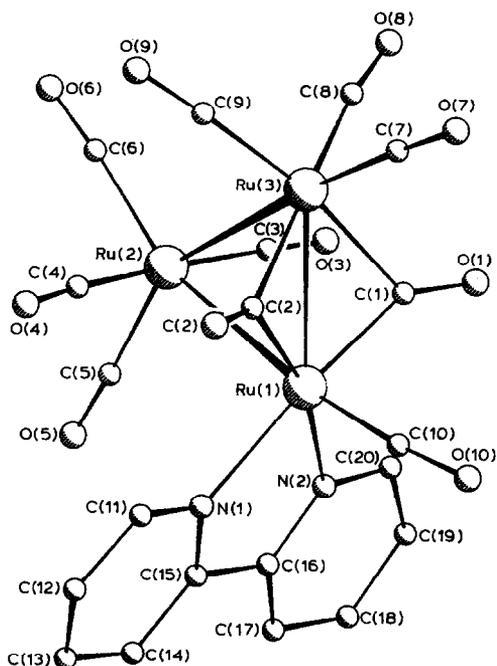
Fig. 1. Plot of a molecule of $Ru_3(\mu\text{-}C\dot{O})_2(CO)_8(\text{bipy})$ (3), showing atom numbering scheme.

groups. The difference in the Ru–C bond distances involving C(1) is 0.254 Å, whereas the difference is only 0.060 Å for those to C(2). The only apparent difference between these two carbonyls is found in the nature of their intermolecular contacts. Whereas the carbonyl C(1)–O(1) does not form any significant intermolecular contacts, a close O(2)...H(12′) (where H(12′) is related to O(2) by the symmetry operation $-1-x$, $1-y$, $-z$) contact of 2.469 Å is found for the other bridging CO ligand.

Complex **3** thus has the $Fe_3(CO)_{12}$-type structure previously found for derivatives of $Ru_3(CO)_{12}$ only in $Ru_3(\mu\text{-}CO)_2(CO)_6\{PPh(OMe)_2\}_4$ [14]. In the phosphonite complex, the Ru–Ru separation bridged by the two CO groups (also asymmetrically) is 2.797(1) Å, similar to that found in **3**. Structurally, **3** is also related to $Fe_2(\mu\text{-}CO)_2(CO)_5(\text{bipy})$ [15], which similarly has two differing asymmetric μ-CO ligands. However, in this case, only one is approximately *trans* to one of the nitrogens of the chelating bipy ligand, whereas in **3**, both μ-CO groups occupy coordination positions approximately *trans* to the nitrogens. In the iron complex, it is considered that the bipy-chelated iron atom donates electron density to the μ-CO π^* orbitals, thus enabling some redistribution of the electron density. A similar mechanism probably operates in the case of **3**, although the final solid-state structure is likely to be determined by intermolecular interactions.

The 2,2′-bipyridyl ligand does not bridge a metal–metal bond as proposed by others [9], but chelates Ru(1) (Ru(1)–N(1) 2.188(4), Ru(1)–N(2) 2.191(5) Å). The Ru_3 plane is almost perpendicular to that of the bipy ligand (dihedral angle 90.2°) and bisects this ligand. In the cyclometallated complex $Os_3(\mu\text{-}H)(\mu\text{-}N_2C_{10}H_7)(CO)_9$

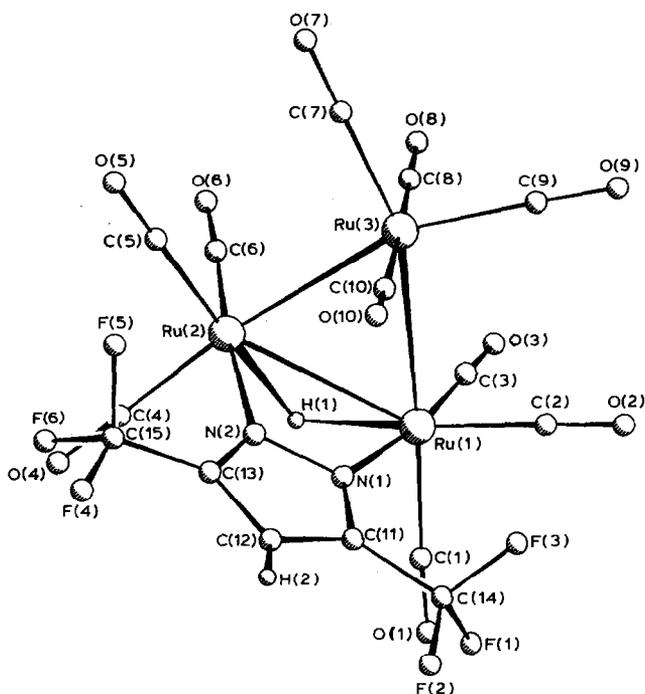Fig. 2. Plot of a molecule of $Ru_3(\mu\text{-H})\{\mu\text{-}H_2C_3H(CF_3)_2\text{-}3,5\}(CO)_{10}$ (7), showing atom numbering scheme.

(4b), the two nitrogen atoms are bonded to one osmium, while the metallated ring is bonded via a Os–C bond to an adjacent osmium atom [16].

The structure of a second crystal modification of this complex has been described briefly [8]; our study has shown no significant differences between the chemically equivalent parameters in the two polymorphs.

Molecular structure of $Ru_3(\mu\text{-H})\{\mu\text{-}N_2C_3H(CF_3)_2\text{-}3,5\}(CO)_{10}$ (7)

Figure 2 shows a molecule of complex 7. The three metal atoms form an isosceles triangle (Ru(1)–Ru(2) 2.902(1), Ru(1)–Ru(3) 2.849(1), Ru(2)–Ru(3) 2.846(1) Å), the longer edge of which is bridged by the hydrogen atom (located during the refinement; Ru–H 1.78, 1.81 Å) and the planar pyrazolide ligand (Ru(1)–N(1) 2.146(3), Ru(2)–N(2) 2.137(3) Å), which is inclined at an angle of 75.4° to the Ru_3 plane. The structure is derived from that of $Ru_3(CO)_{12}$ by replacement of two axial CO groups on adjacent Ru atoms by the pyrazolide group.

The remaining ten CO groups are terminal; the maximum deviation from linearity is found for Ru(3)–C(10)–O(10) (174.3(4)°) where C(10)–O(10) is the axial carbonyl group lying on the same side of the Ru_3 triangle as the pyrazolide ligand. The distortion of the Ru–C–O angle from the ideal 180° is such that the terminal O(10) atom is directed away from the planar pyrazolide ring thereby minimizing possible intramolecular interactions between these ligands. A similar distortion of the comparable carbonyl group is found in the structure of $Ru_3(\mu\text{-}N_2C_4H_4)(CO)_{10}$ in which the mean plane of the 1,2-diazine moiety forms a dihedral angle of 95.1° with the Ru_3 plane [4].

Comparison with osmium. The reaction between $Os_3(CO)_{12}$ and pyridine is complex, four trinuclear and two isomeric binuclear derivatives being isolated from reactions carried out in refluxing octane or in sealed tubes at 184°C [11]. The trinuclear complexes included **1b**, two isomeric forms of $Os_3(\mu\text{-H})(\mu\text{-NC}_5H_4)$-$(CO)_9(py)$, and $Os_3(\mu\text{-H})_2(\mu\text{-NC}_4H_4)_2(CO)_8$ (**2b**). The simple pyridine-substituted complex $Os_3(CO)_{11}(py)$ was formed by rapid displacement of MeCN from $Os_3(CO)_{11}(NCMe)$ [12]. On heating in refluxing octane for a short time, it was converted into the osmium analogue of **1a** with loss of CO. The isolation of the simple substitution product contrasts with the formation of the metallated complex in the analogous ruthenium system, and indicates that once a route is found for the synthesis of the simple substitution product, further transformation of organic molecules is more facile when complexed to a ruthenium cluster than in the osmium analogue.

The reaction between 2,2'-bipyridyl and $Os_3(CO)_{12}$ gives the metallated complex **4b**; no compound analogous to **3** was obtained [16]. The related reaction of $Os_3(CO)_{10}(NCMe)_2$ does not appear to have been described, but might be expected to give the osmium analogue of **3**. The facile conversion of **3** to **4a** by heating in refluxing toluene has been referred to above, although we suggest that the structure of the product is probably analogous to that of the osmium compound, which has been determined by an X-ray study.

Reactions between $Os_3(CO)_{12}$ and pyrazole afford initially a *C*-metallated complex which is converted to the osmium analogue of **5** on heating at 180°C [17]. With 3,5-disubstituted pyrazoles, the analogous *C*-metallated complexes cannot form. We obtained no evidence for the formation of any isomeric *C*-metallated derivative in the ruthenium system.

Conclusion

Reactions between some N-heterocycles and $Ru_3(CO)_{12}$ have given trinuclear complexes which exhibit a variable tendency towards cyclometallation for the pyridine derivatives, and ready formation of the hydrido-pyrazolido complexes for the pyrazoles. Both types of reaction are further examples of oxidative addition of the organic substrate across one of the Ru–Ru bonds of the parent cluster which, in principle at least, can serve to activate the organic molecule toward further reaction.

Experimental

Spectroscopic data were obtained with the following instruments: Perkin–Elmer 457 and Jasco IRA 2 (infrared), Varian Associates T60 (^{1}H NMR) and Bruker WP80 (^{1}H and ^{13}C NMR), AEI-GEC MS3074 (mass). Microanalyses were done by the Canadian Microanalytical Service, Vancouver.

All reactions were carried out under nitrogen although, in general, reaction products were worked up in air. Chromatography was on columns of Florisil or alumina, preparative TLC was on plates (20 × 20 cm) coated with Kieselgel G (Merck). Solvents were dried and distilled before use.

Reactions of Ru₃(CO)₁₂ with nitrogen heterocycles
(a) Pyridine. (i) A mixture of $Ru_3(CO)_{12}$ (300 mg, 0.47 mmol) and pyridine (17.4 ml of a 0.031 *M* solution in tetrahydrofuran, 0.54 mmol) was heated in

refluxing tetrahydrofuran (20 ml) for 2 h. The solvent was removed in vacuo and a light petroleum extract of the residue was concentrated, affording orange crystals of $Ru_3(\mu\text{-H})(\mu\text{-}NC_5H_4)(CO)_{10}$ **(1a)** (257 mg, 83%). Found: C, 26.9; H, 0.7; N, 1.9; M (mass spectrometry) 665; $C_{15}H_5NO_{10}Ru_3$ calcd.: C, 27.2; H, 0.8; N, 2.1%, M 665. IR (cyclohexane): ν(CO) 2103m, 2065vs, 2054vs, 2028m, 2019vs, 2002m, 1990w cm^{-1}. ^{1}H NMR: δ (CDCl$_3$) 7.97, d, J(HH) 5.2 Hz, 1H; 7.25, m, 2H; 6.77, m, 1H; -14.44, s, 1H, RuH.

(ii) A mixture of ruthenium carbonyl (388 mg, 0.61 mmol) and pyridine (288 mg, 3.64 mmol) was refluxed in cyclohexane (150 ml) for 4 h. Evaporation of the solvent and chromatography (alumina) afforded two fractions. A yellow-orange band was eluted with light petroleum. Crystallization (light petroleum) afforded red-orange crystals of $Ru_3(\mu\text{-H})(\mu\text{-}NC_5H_4)(CO)_{10}$ **(1a)** (385 mg, 96%), identified by infrared comparison with the product obtained in (i) above. A second yellow-orange band was eluted with diethyl ether. The product was identified by mass spectrometry as $Ru_3(\mu\text{-H})_2(\mu\text{-}NC_5H_4)_2(CO)_8$ **(2a)** (Found: M (mass spectrometry), 688. $C_{18}H_{10}N_2O_8Ru_3$ calcd.: M, 688). IR (cyclohexane): ν(CO) 2080w, 2047s, 2039s, 1998s, 1992(sh), 1990m, and 1986m cm^{-1}.

(b) 2,2'-Bipyridyl. A mixture of ruthenium carbonyl (300 mg, 0.47 mmol) and 2,2'-bipyridyl (bipy) (73 mg, 0.47 mmol) was refluxed in cyclohexane (100 ml) for 20 min. The purple crystals that deposited were collected, washed with light petroleum and dried in air for a short period to give pure $Ru_3(CO)_{10}$(bipy) **(3)** (320 mg, 92%)

TABLE 1

SUMMARY OF CRYSTALLOGRAPHIC DATA FOR 3 AND 7

	3	7
Formula	$C_{20}H_8N_2O_{10}Ru_3$	$C_{15}H_2F_6N_2O_{10}Ru_3$
M	739.5	787.4
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
	$(C_{2h}^5,\text{No.14})$	$(C_{2h}^5,\text{No. 14})$
a, Å	7.834(2)	16.802(3)
b, Å	25.818(2)	7.726(1)
c, Å	11.717(1)	18.807(3)
β, deg	107.41(1)	114.24(1)
U, Å^3	2261.3	2261.1
D_m, g cm^{-3}	2.17	2.34
Z	4	4
D_x, g cm^{-3}	2.172	2.349
μ(Mo-K_α), cm^{-1}	19.7	20.39
$F(000)$	1416	1488
θ range	$1 < \theta < 25°$	$1 < \theta < 25°$
Reflections meas.	5494	5073
Unique reflections	4409	3900
Reflections with		
$I > 2.5\sigma(I)$	3336	2993
R	0.031	0.025
k	1.00	2.46
g	0.0049	0.0003
R_w	0.034	0.026

(Found: C, 31.9; H, 1.4; N, 4.0. $C_{20}H_8N_2O_{10}Ru_3$ calcd.: C, 32.5; H, 1.1; N, 3.8%). IR (CHCl$_3$): ν(CO) 2077m, 2034s, 1994s, and 1740vw cm^{-1}.

(c) Pyrazole. A mixture of Ru$_3$(CO)$_{12}$ (200 mg, 0.31 mmol) and pyrazole (24 mg, 0.358 mmol) was heated in refluxing cyclohexane (25 ml) for 2 h. The solvent was removed by rotary evaporation and a dichloromethane extract of the residue was chromatographed (silica TLC plates/light petroleum eluant), affording six bands. Multiple development of the chromatography plates was necessary to purify band 3, orange, which was crystallized (dichloromethane/methanol) and identified as Ru$_3$(μ-H)(μ-N$_2$C$_3$H$_3$)(CO)$_{10}$ (5) (30 mg, 15%), m.p. 170–175°C (dec.). Found: C, 24.01; H, 0.43; N, 4.10, M (mass spectrometry) 653; C$_{13}$H$_4$N$_2$O$_{10}$Ru$_3$ calcd.: C, 23.97; H, 0.62; N, 4.30%; M 653. IR (cyclohexane): ν(CO) 2109m, 2072vs, 2066vs,

TABLE 2

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ FOR Ru, $\times 10^4$ FOR OTHER ATOMS) FOR Ru$_3$(μ-CO)$_2$(CO)$_8$(bipy) (3)

Atom	x	y	z
Ru(1)	−37782(5)	38109(1)	22823(3)
Ru(2)	−2158(6)	36817(2)	38255(4)
Ru(3)	−30561(6)	30263(2)	39558(4)
C(1)	−3700(7)	3065(2)	1982(5)
O(1)	−3858(6)	2751(2)	1250(4)
C(2)	−4290(8)	3748(2)	3876(5)
O(2)	−4968(6)	4008(2)	4448(4)
C(3)	53(8)	3193(2)	2630(6)
O(3)	283(8)	2920(2)	1938(5)
C(4)	−870(8)	4152(3)	4917(6)
O(4)	−1136(9)	4437(2)	5573(6)
C(5)	780(9)	4238(2)	3144(6)
O(5)	1319(8)	4574(2)	2737(5)
C(6)	1798(8)	3398(2)	5085(5)
O(6)	2997(6)	3261(2)	5814(4)
C(7)	−5194(9)	2661(2)	3948(6)
O(7)	−6416(7)	2438(2)	4013(5)
C(8)	−1781(9)	2399(2)	3778(5)
O(8)	−1145(8)	2021(2)	3655(5)
C(9)	−2092(10)	3095(2)	5657(6)
O(9)	−1512(11)	3145(2)	6660(4)
C(10)	−6234(8)	3798(2)	1426(5)
O(10)	−7705(7)	3767(2)	905(5)
N(1)	−3591(6)	4657(2)	2325(4)
N(2)	−2874(6)	4038(2)	757(4)
C(11)	−4029(8)	4957(2)	3151(5)
C(12)	−3889(8)	5489(2)	3168(6)
C(13)	−3281(9)	5725(2)	2306(6)
C(14)	−2835(8)	5434(2)	1475(6)
C(15)	−3038(7)	4889(2)	1475(5)
C(16)	−2682(7)	4543(2)	588(4)
C(17)	−2153(8)	4716(2)	−401(5)
C(18)	−1849(9)	4375(2)	−1192(5)
C(19)	−2071(9)	3857(2)	−1016(5)
C(20)	−2596(8)	3698(2)	−54(5)

2030vs, 2016s, 1999(sh), 1997m, 1985w, 1974w, 1967w cm^{-1}. ^{1}H NMR: δ (CDCl$_3$) -13.44, s, 1H, RuH; 6.2, t, J(HH) 2.2 Hz, 1H, H(4); 7.50, d, J(HH) 2.2 Hz, 2H, H(3) + H(5). About 40 mg of a mixture of Ru$_3$(CO)$_{12}$ and Ru$_4(\mu$-H)$_4$(CO)$_{12}$ was also recovered by chromatography.

(d) 3,5-Dimethylpyrazole. A mixture of Ru$_3$(CO)$_{12}$ (200 mg, 0.31 mmol) and 3,5-dimethylpyrazole (31 mg, 0.32 mmol) was heated in refluxing cyclohexane for 16 h. The solvent was removed (rotary evaporator) and a dichloromethane extract of the residue was chromatographed (silica TLC plates/light petroleum eluant) affording five bands. As in (c), rechromatography proved necessary. Band 1, yellow, was identified as Ru$_4(\mu$-H)$_4$(CO)$_{12}$ (5 mg, 9%). Band 2, orange, was crystallized

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^5$ FOR Ru, $\times 10^4$ FOR OTHER ATOMS) FOR Ru$_3(\mu$-H)$\{\mu$-N$_2$C$_3$H(CF$_3$)$_2\}$(CO)$_{10}$ (7)

Atom	x	y	z
Ru(1)	82127(2)	29589(4)	35977(2)
Ru(2)	73105(2)	30386(4)	19103(2)
Ru(3)	84067(2)	58317(4)	27320(2)
C(1)	8059(3)	900(6)	4130(3)
O(1)	8019(3)	−270(5)	4463(3)
C(2)	8668(3)	4447(6)	4492(3)
O(2)	8971(3)	5265(5)	5033(2)
C(3)	9353(3)	2282(6)	3768(3)
O(3)	10036(2)	1819(5)	3874(2)
C(4)	6618(3)	990(6)	1459(2)
O(4)	6249(2)	−252(5)	1206(2)
C(5)	6796(3)	4604(6)	1041(3)
O(5)	6522(2)	5487(5)	521(2)
C(6)	8170(3)	2442(6)	1547(3)
O(6)	8661(2)	2063(5)	1307(2)
C(7)	8243(3)	7300(6)	1859(3)
O(7)	8140(3)	8162(5)	1340(2)
C(8)	9397(3)	4734(6)	2631(3)
O(8)	9985(2)	4215(5)	2562(2)
C(9)	9185(3)	7233(6)	3582(3)
O(9)	9649(3)	8031(5)	4089(2)
C(10)	7365(3)	6797(6)	2806(3)
O(10)	6792(2)	7473(5)	2834(2)
N(1)	6864(2)	3635(4)	3232(2)
N(2)	6445(2)	3659(4)	2447(2)
C(11)	6266(3)	3959(6)	3519(2)
C(12)	5463(3)	4228(6)	2928(3)
C(13)	5597(3)	4024(6)	2260(2)
C(14)	6507(3)	4108(7)	4366(3)
C(15)	4955(3)	4221(7)	1439(3)
F(1)	6973(3)	2774(6)	4769(2)
F(2)	5803(2)	4198(5)	4515(2)
F(3)	6994(3)	5480(5)	4687(2)
F(4)	4156(2)	4461(5)	1403(2)
F(5)	5117(2)	5622(4)	1100(2)
F(6)	4932(2)	2917(5)	985(2)

(dichloromethane/methanol) and identified as $Ru_3(\mu\text{-H})(\mu\text{-}N_2C_3HMe_2\text{-}3,5)(CO)_{10}$ (**6**) (44 mg, 21%), m.p. 143–147°C. Found: C, 26.63; H, 1.09; N, 4.12%; M (mass spectrometry) 681. $C_{15}H_8N_2O_{10}Ru_3$ calcd.: C, 26.52; H, 1.12; N, 4.12%; M 681. IR (cyclohexane): ν(CO) 2108m, 2068vs, 2063vs, 2029vs, 2019m, 2010s, 1998m, 1994m, 1980w, 1971w, 1966w cm^{-1}. ^{1}H NMR: δ (CDCl$_3$) -13.23, s, 1H, RuH; 2.04, s, 6H, Me; 5.72, s, 1H, H(4).

(e) 3,5-Bis(trifluoromethyl)pyrazole. A mixture of $Ru_3(CO)_{12}$ (200 mg, 0.31 mmol) and 3,5-bis(trifluoromethyl)pyrazole (142 mg, 0.70 mmol) was heated in refluxing cyclohexane (25 ml) for 3.5 h, after which time solvent was removed (rotary evaporator). Addition of methanol to a filtered dichloromethane extract of the residue, followed by concentration afforded orange crystals of $Ru_3(\mu\text{-H})\{\mu\text{-}N_2C_3H(CF_3)_2\text{-}3,5\}(CO)_{10}$ (**7**) (202 mg, 82%), m.p. 127–131°C. Found: C, 22.78; H, < 0.2; N, 3.20, M (mass spectrometry) 789; $C_{15}H_2F_6N_2O_{10}Ru_3$ calcd.: C, 22.88, H, 0.26; N, 3.56%, M 789. IR (cyclohexane) ν(CO) 2116m, 2083vs, 2071vs, 2033vs, 2016m, 2006m, 1978w cm^{-1}. ^{1}H NMR: δ (CDCl$_3$) -13.16, s, 1H, RuH; 6.78, s, 1H, H(4).

Crystallography

Crystals suitable for X-ray diffraction studies of **3** were grown by vapour diffusion of Et$_2$O into a CH$_2$Cl$_2$ solution of the compound; crystals of **7** were grown by liquid diffusion of MeOH into a CH$_2$Cl$_2$ solution. Intensity data for compounds **3** and **7** were collected on an Enraf–Nonius CAD4-F diffractometer fitted with Mo-K_α (graphite monochromator) radiation, λ 0.71073 Å, with the use of the $\omega/2\theta$ scan technique. No decomposition of either crystal occurred during their respective data collections. Corrections were applied for Lorentz and polarization effects using the program SUSCAD [18] for **3** and PREABS and PROCES [18]

TABLE 4

BOND DISTANCES (Å) FOR $Ru_3(\mu\text{-CO})_2(CO)_8$(bipy) (**3**)

Ru(2)–Ru(1)	2.855(1)	Ru(3)–Ru(1)	2.757(1)
C(1)–Ru(1)	1.963(5)	C(2)–Ru(1)	2.029(6)
C(10)–Ru(1)	1.885(6)	N(1)–Ru(1)	2.188(4)
N(2)–Ru(1)	2.191(5)	Ru(3)–Ru(2)	2.836(1)
C(3)–Ru(2)	1.942(7)	C(4)–Ru(2)	1.942(7)
C(5)–Ru(2)	1.918(7)	C(6)–Ru(2)	1.951(5)
C(1)–Ru(3)	2.217(6)	C(2)–Ru(3)	2.089(5)
C(7)–Ru(3)	1.920(7)	C(8)–Ru(3)	1.947(7)
C(9)–Ru(3)	1.917(6)	O(1)–C(1)	1.159(7)
O(2)–C(2)	1.180(8)	O(3)–C(3)	1.129(9)
O(4)–C(4)	1.125(10)	O(5)–C(5)	1.132(9)
O(6)–C(6)	1.122(7)	O(7)–C(7)	1.140(9)
O(8)–C(8)	1.124(9)	O(9)–C(9)	1.134(8)
O(10)–C(10)	1.134(8)	C(11)–N(1)	1.362(8)
C(15)–N(1)	1.341(8)	C(16)–N(2)	1.335(7)
C(20)–N(2)	1.358(8)	C(12)–C(11)	1.378(8)
C(13)–C(12)	1.380(10)	C(14)–C(13)	1.357(10)
C(15)–C(14)	1.416(7)	C(16)–C(15)	1.459(8)
C(17)–C(16)	1.414(9)	C(18)–C(17)	1.350(9)
C(19)–C(18)	1.373(9)	C(20)–C(19)	1.373(9)

TABLE 5

BOND DISTANCES (Å) FOR $Ru_3(\mu\text{-H})\{\mu\text{-}N_2C_3H(CF_3)_2\}(CO)_{10}$ (7)

Ru(2)–Ru(1)	2.902(1)	Ru(3)–Ru(1)	2.849(1)
H(1)–Ru(1)	1.811(–)	C(1)–Ru(1)	1.953(5)
C(2)–Ru(1)	1.918(5)	C(3)–Ru(1)	1.882(5)
N(1)–Ru(1)	2.146(3)	Ru(3)–Ru(2)	2.846(1)
H(1)–Ru(2)	1.784(–)	C(4)–Ru(2)	1.942(5)
C(5)–Ru(2)	1.929(5)	C(6)–Ru(2)	1.891(5)
N(2)–Ru(2)	2.137(3)	C(7)–Ru(3)	1.921(5)
C(8)–Ru(3)	1.945(5)	C(9)–Ru(3)	1.929(5)
C(10)–Ru(3)	1.958(5)	O(1)–C(1)	1.118(5)
O(2)–C(2)	1.126(5)	O(3)–C(3)	1.139(5)
O(4)–C(4)	1.135(5)	O(5)–C(5)	1.124(5)
O(6)–C(6)	1.130(5)	O(7)–C(7)	1.134(6)
O(8)–C(8)	1.121(5)	O(9)–C(9)	1.135(5)
O(10)–C(10)	1.115(5)	N(2)–N(1)	1.351(4)
C(11)–N(1)	1.343(5)	C(13)–N(2)	1.350(5)
C(12)–C(11)	1.366(6)	C(14)–C(11)	1.479(6)
H(12)–C(12)	0.997(4)	C(13)–C(12)	1.374(6)
C(15)–C(13)	1.485(6)	F(1)–C(14)	1.327(6)
F(2)–C(14)	1.325(5)	F(3)–C(14)	1.324(6)
F(4)–C(15)	1.329(5)	F(5)–C(15)	1.339(6)
F(6)–C(15)	1.311(6)		

for 7; in addition an absorption correction was applied for 7 (max. and min. transmission factors 0.7880 and 0.7178). Relevant crystal data are summarized in Table 1.

Both structures were solved by direct method [18] and refined by a full-matrix least-squares method. Anisotropic thermal parameters were introduced for all non-hydrogen atoms. For 3, hydrogen atoms were included at their calculated positions and for 7, were located from a difference map. A weighting scheme, $w = k/[\sigma^2(F) + g \, | \, F \, |^2]$, was introduced and the refinement continued until convergence. For 3, the maximum residual electron density peak was 0.49 e$Å^{-3}$ and for 7 0.64 e$Å^{-3}$. The analyses of variance showed no special features for both models. The scattering factors for neutral Ru were from ref [19] while those for the remaining atoms were those incorporated in SHELX [18].

Fractional atomic coordinates and bond distances are listed for complex 3 in Tables 2 and 4 and for complex 7 in Tables 3 and 5.

Acknowledgement

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