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The synthesis of some binuclear ruthenium(I) complexes bridged by anionic groups. X-ray structures of pyrazolate- and oxypyridinate-bridged complexes

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Abstract

A series of binuclear ruthenium(I) complexes, $[Ru_2(CO)_4(\mu\text{-}XY)_2(PPh_3)_2]$, have been prepared by two closely related routes. Complexes **2** ($XY^- = S_2NC_3H_4^-$) and **3** ($XY^- = NC_5H_4O^-$) have been prepared by the reaction of $[Ru_2(CO)_4(O_2CCH_3)_2(PPh_3)_2]$ with sodium 2-mercaptothiazolinate and sodium 2-oxypyridinate, respectively. The related pyrazolate-bridged complex **4** ($XY^-=N_2C_3H_3^-$) was prepared by the reaction of sodium pyrazolate with $[Ru_2(CO)_4(O_2CCH_3)(NCMe)_2]$ followed by addition of PPh_3. The X-ray structures of compounds **3** and **4** have been determined. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with a 14.766(2), b 15.821(2), c 10.745(3) Å, α 98.28(2)°, β 110.99(2)°, γ 103.29(1)°, V 2209.1 Å^3, $Z = 2$. On the basis of 5521 unique observations (NO) and 379 parameters varied (NV) the structure has been refined to $R = 0.042$ and $R_w = 0.054$. Compound **4** crystallizes in the orthorhombic space group $P2_12_12_1$ with a 13.220(2), b 14.846(4), c 21.403(3) Å, V 4200.7 Å^3 and $Z = 4$. This structure has been refined to $R = 0.041$ and $R_w = 0.023$ for $NO = 3915$ and $NV = 546$. Both structures display the sawhorse arrangement of carbonyl groups and have the phosphine ligands in the axial positions opposite the Ru–Ru bonds. For **3** the oxypyridinate groups are bound in a head-to-tail arrangement. The two-atom pyrazolate bridge imparts more strain than the three-atom oxypyridinate bridge and as a result the equatorial planes of the Ru centers are tipped by only 16.2(4)° in **3** but by 35.4(1)° in **4**. The Ru–Ru distances (2.7108(4) Å (**3**); 2.732(1) Å (**4**)) correspond to normal single bonds.

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Introduction

Until recently the chemistry of binuclear Ru^I complexes has largely been limited to that involving $[CpRu(CO)_2]_2$ and related species [1*], and the carboxylate-bridged dimers, $[Ru(CO)_2(\mu\text{-}O_2CR)L]_2$ [2]. However two recent developments have significantly extended the known types of Ru^I dimers. A series of pyrazolyl-bridged Ru^I complexes of the type $[Ru(CO)_3(\mu\text{-}Pz)]_2$ has been reported by Oro and coworkers [3], and we have synthesized three classes of binuclear Ru^I complexes, $[Ru(CO)_2(\mu\text{-}O_2CMe)(\eta^1\text{-}Ph_2PCH_2PPh_2)]_2$ and $[Ru_2(CO)_4(\mu\text{-}O_2CMe)(\eta^2\text{-}Ph_2P(CH_2)_nPPh_2)_2]^+$ ($n = 1$ and 2), in which the diphosphines are either pendant, bridging ($n = 1$), or chelating ($n = 2$) [4].

In related chemistry of Rh and Ir two principal strategies have been used for preserving the binuclear integrity of the complexes during the reactions while still allowing flexibility of the bimetallic framework. These involved the use of either neutral diphosphines [5*] or related groups [6*], or anionic ligands [7–14] to bridge the metals, holding them in close proximity. Both of these strategies have recently been successfully applied to Ru^I chemistry; that involving diphosphines is the subject of a recent report [4], and in this paper we report a new class of binuclear Ru^I complexes bridged by anionic groups. These latter complexes are not unlike the pyrazolyl-bridged species reported by Oro [3], whose work appeared while our study was underway, and also resemble a mercaptobenzothiazolinate-bridged complex reported earlier [15].

Experimental

General comments.

All solvents were appropriately dried and distilled prior to use under a dinitrogen atmosphere and all manipulations were routinely carried out under N_2 using Schlenk conditions. The compounds 2-mercaptothiazoline, 2-hydroxypyridine and triphenylphosphine were obtained from Aldrich. Sodium hydride as a 60% oil emulsion was obtained from Aldrich and stored under dinitrogen; before use it was refluxed in toluene for 3 h, washed with hexanes, dried, and stored under dinitrogen. The complexes $[Ru(CO)_2(O_2CCH_3)]_n$ and $[Ru(CO)_2(O_2CCH_3)(CH_3CN)]_2$ (**1a**) were prepared by literature methods [2]. IR spectra were recorded on either Nicolet 7199 or Mattson Polaris FT spectrometers with use of Nujol mulls on KBr plates or in solution in NaCl cells. $^{31}P\{^1H\}$ NMR spectra were recorded on either Bruker HFX-90 (operating at 36.4 MHz), AM-300 (at 121.5 MHz) or WH-400 (at 161.4 MHz) spectrometers, while ^1H NMR spectra were recorded on the AM-300 or WH-400 spectrometers. Elemental analyses were performed within the respective departments at the University of Alberta and CSIR, Pretoria.

Preparation of compounds

(a) Sodium 2-oxypyridinate. One gram (10.5 mmol) of 2-hydroxypyridine was partially dissolved in THF (7 ml) and one equivalent of sodium hydride (252 mg; 10.5 mmol) was slowly added resulting in dihydrogen evolution and the precipita-

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Spectroscopic data for the compounds, $[Ru(CO)_2(\mu\text{-}XY)(PPh_3)]_2$

XY	IR (cm^{-1}) [a]		NMR [b] (ppm)	
	solid	solution	$^{31}P\{^1H\}$ [b,c]	^1H
O_2CCH_3 (**1**)	2109s, 1977m, 1943s, 1912w, 1571s, 1432m	2025s, 1978m, 1957sh, 1948s, 1914w, 1571s, 1432m [c]	13.70s [d]	7.49 (m, 10H) [e,d] 7.35 (m, 20H) 1.74 (s, 6H)
$S_2NC_3H_4$ (**2**)	2018s, 1977m, 1947s, 1928w 1588sh, 1571m, 1550sh	2020s, 1981m, 1952s, 1928w, 1583sh, 1570m, 1540sh	14.54s [g]	7.50 (m, 10H) [g] 7.39 (m, 20H) 3.67 (m, 2H) 3.46 (m, 2H) 2.89 (m, 4H)
NC_5H_4O (**3**)	2017s, 1971m, 1946s, 1914w, 1610m, 1600sh, 1542w	2019s, 1978m, 1946s, 1917w, 1611m, 1600sh 1543w [f]	13.24s [f]	7.53 (m, 12H) [f] 7.35 (m, 20H) 7.09 (m, 2H) 6.08(d, 2H, *J* 8.0 Hz) 5.75 (m, 2H)
$N_2C_3H_3$ (**4**)	2022s, 1982m, 1961s, 1930sh, 1481m, 1434m	2024s, 1983m, 1956s, 1481w, 1435m, 1381w	19.76s [g,h]	7.55 (m, 12H) [g,h] 7.41 (t, 6H, *J* 7.0 Hz) 7.37 (t, 12H, *J* 7.1 Hz) 6.62 (d, 4H, *J* 1.9 Hz) 5.69 (t, 2H, *J* 1.9 Hz)

[a] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder (IR); s, singlet; d, doublet; t, triplet; m, multiplet (NMR). [b] Obtained at 20 °C, on a Bruker WH400 unless otherwise noted. [c] THF. [d] C_6D_6. [e] Obtained on a Varian 80 MHz instrument. [f] CH_2Cl_2 (IR)/CD_2Cl_2 (NMR). [g] $CDCl_3$. [h] Spectrum was obtained at 30 °C on an AM-300 instrument, operating at 121 MHz for phosphorous.

tion of a white solid. The mixture was stirred for 30 min, the solvent volume was reduced to ca. 1–2 ml under a nitrogen stream and Et_2O (15 ml) was added to induce complete crystallization. The white salt was filtered, washed with Et_2O (2 × 5 ml) and dried in vacuo giving nearly quantitative yields. Anal. Found: C, 50.46; H, 3.55; N, 11.8. C_5H_4NONa calcd.: C, 51.28; H, 3.42; N, 11.97%.

The sodium salts of 2-mercaptothiazolinate and pyrazolate were obtained in this manner starting from 2-mercaptothiazoline and pyrazole.

(b) $[Ru_2(CO)_4(O_2CCH_3)_2(PPh_3)_2]$ (1b). $[Ru_2(CO)_4(O_2CCH_3)_2(CH_3CN)_2]$ (**1a**) (118.2 mg; 0.23 mmol) was dissolved in THF (5 ml) producing an orange solution. A solution of PPh_3 (121 mg; 0.46 mmol) in THF (3 ml) was added resulting in an immediate color change to yellow. The reaction mixture was allowed to stir for 30 min and a $^{31}P\{^1H\}$ NMR spectrum at this stage revealed the presence of only one symmetrical species. Reduction of the solvent volume to ca. 1–2 ml followed by addition of EtOH (15 ml) produced a yellow crystalline solid. The solid was collected, washed with Et_2O (2 × 5 ml) and dried in air (yield 196 mg, 89%). Anal. Found: C, 54.90; H, 3.66. $C_{44}H_{36}O_8P_2Ru_2$ calcd.: C, 55.23; H, 3.79%. The spectroscopic data obtained for **1** were similar to that obtained previously by a different route [2]. See Table 1 for spectroscopic details for this and other compounds.

(c) $[Ru_2(CO)_4(S_2NC_3H_4)_2(PPh_3)_2]$ (2). A THF solution (2 ml) of sodium 2-mercaptothiazolinate (65.4 mg; 0.46 mmol) was added to a solution containing $[Ru_2(CO)_4(O_2CCH_3)_2(PPh_3)_2]$ (**1b**) (219.9 mg; 0.23 mmol) in THF (5 ml), resulting in an immediate color change to orange followed by a clouding of the solution

due to the precipitation of sodium acetate. The mixture was gently heated for 2 h and the solvent was removed under a nitrogen stream leaving a yellow-orange solid which was taken up in CH_2Cl_2 and filtered. Addition of ether to the CH_2Cl_2 solution gave the required product **2** in 85% yield (210 mg). Anal. Found: C, 50.64; H, 3.83; N, 2.52; S, 11.83. $C_{46}H_{38}N_2O_4P_2Ru_2S_4$ calcd.: C, 51.39; H, 3.56; N, 2.61; S, 11.93%.

(d) $[Ru_2(CO)_4(NC_5H_4O)_2(PPh_3)_2]$ *(3).* Sodium 2-oxypyridinate (53.8 mg; 0.46 mmol), dissolved in CH_2Cl_2 (4 ml) and MeOH (1 ml), was added to a THF solution (7 ml) containing $[Ru_2(CO)_4(O_2CCH_3)_2(PPh_3)_2]$ (220 mg; 0.23 mmol). The color of the solution immediately darkened and became cloudy due to the precipitation of sodium acetate. The solvent was removed after 4 h, leaving a yellow crystalline solid. Dissolution in CH_2Cl_2 (15 ml) was followed by filtration to remove sodium acetate and concentration to ca. 1–2 ml. Addition of Et_2O (15 ml) afforded the product in 95% yield (224 mg). Anal. Found: C, 58.15; H, 3.87; N, 2.86. $C_{50}H_{38}N_2O_6P_2Ru_2$ calcd.: C, 58.48; H, 3.73; N, 2.73%.

(e) $[Ru_2(CO)_4(N_2C_3H_3)_2(PPh_3)_2]$ *(4).* The addition of sodium pyrazolate (270 mg; 3.0 mmol) in MeOH (10 ml) to $[Ru_2(CO)_4(O_2CCH_3)_2(NCMe)_2]$ (260 mg; 0.50 mmol), dissolved in MeOH (20 ml), produced an immediate color change from orange to light yellow. Addition of PPh_3 (300 mg; 1.1 mmol) to the stirred solution and subsequent heating for 2 h under reflux resulted in the formation of the pale yellow microcrystalline product in 62% yield (300 mg). The compound was recrystallized from CH_2Cl_2/EtOH. Anal. Found: C, 55.92; H, 3.39; N, 5.67. $C_{46}H_{36}N_4O_4P_2Ru_2$ calcd.: C, 56.79; H, 3.73; N, 5.75%.

X-ray data collection

Suitable yellow crystals of **3** were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex and pale yellow crystals of **4** were obtained from CH_2Cl_2/EtOH. Data for both compounds were collected on Enraf–Nonius CAD4 diffractometers using graphite-monochromated Mo-K_α radiation. The automatic peak search and reflection indexing programs, in conjunction with a cell reduction program, established the crystal systems. For compound **3** the lack of absences and the triclinic symmetry of the cell established the space group as either $P1$ or $P\bar{1}$, the latter of which was confirmed by the successful refinement of the structure. For **4** the orthorhombic cell and the systematic absences ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) unambiguously defined the space group as $P2_12_12_1$. Cell constants for both compounds were obtained from least-squares refinements of the setting angles of 25 reflections having 2θ between 22.0° and 26.0° for **3** and between 14.0° and 34.0° for **4**.

The intensity data for **3** were collected by using $\theta/2\theta$ scans, and for **4** were collected using ω scans, employing variable speeds chosen to give $\sigma(I)/I \leqslant 0.3$ within a time limit of 50 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the α_1–α_2 wavelength dispersion, and backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range. Three reflections were chosen as standard reflections and were remeasured every 60 min of exposure time to check on crystal stability over the course of data collection. For both compounds no significant variation in the standards was noted so no correction was applied. See Table 2 for crystal data and

Table 2

Crystal data and details of intensity collection for compounds **3** and **4**

Compound	$Ru_2(CO)_4(\mu\text{-}NC_5H_4O)_2(PPh_3)_2$ (**3**)	$Ru_2(CO)_4(\mu\text{-}N_2C_3H_3)_2(PPh_3)_2$ (**4**)
Formula	$C_{50}H_{38}N_2O_6P_2Ru_2$	$C_{46}H_{36}O_4N_4P_2Ru_2$
FW	1026.96	972.91
Cell Parameters		
a (Å)	14.766(2)	13.220(2)
b (Å)	15.821(2)	14.846(4)
c (Å)	10.745(3)	21.403(3)
α (°)	98.28(2)	90.00
β (°)	110.99(2)	90.00
γ (°)	103.29(1)	90.00
V (Å^3)	2209.1	4200.7
Space Group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)
Z	2	4
ρ(calcd)	1.54	1.54
Temp. (°C)	295°K	293°K
Radiation (λ, Å)	Mo (0.71073)	Mo (0.71073)
Receiving aperture, mm	2.00(1.00 tan θ) wide × 4.00 high	173 from crystal
Scan type	$\theta/2\theta$	ω
Scan speed (deg min^{-1})	1.54–6.67	0.78–3.30
Scan width, deg	0.70 + (0.347 tan θ) in θ	0.49 + (0.347 tan θ)
No. of unique data collected	7723	4135
Two θ maximum, deg	50.0	50.0
No. of unique observations	5521 ($F_o^2 > 3\sigma(F_o^2)$)	3915 ($F_o^2 > \sigma(F_o^2)$)
Crystal shape	Parallelpiped	Cube
Crystal dimensions (mm)	0.30 × 0.25 × 0.15	0.30 × 0.30 × 0.30
Absorption coefficient (cm^{-1})	7.92	7.48
Final number of parameters	379	546
Error in observation of unit weight	1.620	[c]
R [a]	0.0419	0.0413
R_w [b]	0.0538	0.0231

[a] $R = \frac{\Sigma \| F_o| - |F_c\|}{\Sigma |F_o|}$. [b] $R_w = [\frac{[\Sigma w(|F_o| - |F_c|)]^2}{\Sigma w F_o^2}]^{1/2}$. [c] For compound **4** a fixed weighting scheme was used with k determined as 0.2386 for $w = \frac{k}{\sigma^2(F_o)}$.

details of intensity collection. The data were corrected for Lorentz and polarization effects and for absorption by the method of Walker and Stuart [16] for compound **3** and by the method of North, Phillips and Matthews [17] for compound **4**. Data were reduced in the usual manner by using a value of $p = 0.04$ to down-weight intense reflections [18].

Structure solution and refinement Both structures were solved by using Patterson techniques to locate the metal atoms, and subsequent least-squares and difference Fourier calculations [19*] to obtain the other atom positions. All hydrogen atoms were placed in their idealized positions using C–H distances of 0.95 Å for **3**; the hydrogen thermal parameters of **3** were fixed at 1.20 times those of the attached carbon atoms, whereas for compound **4** common thermal parameters (B's) refined

Table 3

Positional and isotropic thermal parameters for $[Ru(CO)_2(\mu\text{-}NC_5H_4O)(PPh_3)]_2$ (3)

Atom	x	y	z	B (Å^2) [a]
Ru(1)	0.38872(3)	0.23269(3)	0.15010(4)	2.379(8)
Ru(2)	0.19919(3)	0.22529(3)	−0.02212(4)	2.553(9)
P(1)	0.54955(9)	0.24455(8)	0.3360(1)	2.43(3)
P(2)	0.03867(9)	0.24487(9)	−0.1690(1)	2.77(3)
O(1)	0.4595(3)	0.1754(3)	−0.0665(4)	6.4(1)
O(2)	0.3120(3)	0.0394(2)	0.1500(4)	4.8(1)
O(3)	0.2743(3)	0.2336(4)	−0.2469(4)	6.3(1)
O(4)	0.1218(4)	0.0255(3)	−0.1237(5)	6.7(2)
O(5)	0.3392(2)	0.2824(2)	0.2983(3)	2.75(8)
O(6)	0.2573(2)	0.3649(9)	0.0664(3)	2.96(8)
N(1)	0.1682(3)	0.2204(3)	0.1595(4)	3.0(1)
N(2)	0.4246(3)	0.3702(3)	0.1310(4)	3.1(1)
C(1)	0.4315(4)	0.1966(4)	0.0171(5)	3.9(1)
C(2)	0.3417(4)	0.1150(3)	0.1521(5)	3.2(1)
C(3)	0.2456(4)	0.2305(4)	−0.1601(5)	3.8(1)
C(4)	0.1513(4)	0.1023(4)	−0.0849(6)	4.0(1)
C(5)	0.0729(4)	0.1873(4)	0.1550(6)	4.6(2)
C(6)	0.0507(4)	0.1945(5)	0.2690(6)	5.3(2)
C(7)	0.1307(4)	0.2368(4)	0.3967(6)	4.8(1)
C(8)	0.2260(4)	0.2671(4)	0.4052(5)	3.6(1)
C(9)	0.2461(3)	0.2568(3)	0.2854(5)	2.6(1)
C(10)	0.5216(4)	0.4216(4)	0.1572(6)	4.6(2)
C(11)	0.5482(5)	0.5131(5)	0.1742(7)	5.7(2)
C(12)	0.4748(5)	0.5565(4)	0.1646(7)	5.5(2)
C(13)	0.3780(4)	0.5050(4)	0.1315(6)	4.2(1)
C(14)	0.3513(4)	0.4116(3)	0.1093(5)	2.9(1)
C(21)	0.5404(3)	0.1804(3)	0.4628(5)	2.73(9) [b]
C(22)	0.4692(4)	0.1892(4)	0.5149(6)	4.3(1)
C(23)	0.4668(5)	0.1532(5)	0.6265(7)	5.2(1)
C(24)	0.5337(4)	0.1080(4)	0.6808(6)	4.8(1)
C(25)	0.6021(4)	0.0969(4)	0.6271(6)	4.7(1)
C(26)	0.6077(4)	0.1336(4)	0.5179(6)	4.0(1)
C(31)	0.6327(3)	0.3521(3)	0.4560(5)	2.59(9)
C(32)	0.5934(4)	0.4228(4)	0.4667(5)	3.7(1)
C(33)	0.6543(4)	0.5038(4)	0.5644(6)	4.5(1)
C(34)	0.7513(4)	0.5140(4)	0.6485(6)	4.7(1)
C(35)	0.7901(4)	0.4419(4)	0.6402(6)	4.6(1)
C(36)	0.7307(4)	0.3623(4)	0.5432(6)	4.1(1)
C(41)	0.6301(3)	0.2005(3)	0.2660(5)	2.79(9)
C(42)	0.7095(4)	0.2566(4)	0.2489(6)	4.1(1)
C(43)	0.7628(5)	0.2202(5)	0.1800(7)	5.7(2)
C(44)	0.7348(5)	0.1291(5)	0.1299(7)	5.7(2)
C(45)	0.6565(5)	0.0743(5)	0.1437(7)	5.9(2)
C(46)	0.6016(4)	0.1096(4)	0.2099(6)	4.4(1)
C(51)	0.0544(4)	0.3205(3)	−0.2797(5)	3.2(1)
C(52)	−0.0241(4)	0.3148(4)	−0.4028(6)	4.7(1)
C(53)	−0.0103(5)	0.3730(5)	−0.4848(7)	5.9(2)
C(54)	0.0816(5)	0.4360(5)	−0.4447(7)	5.7(2)
C(55)	0.1590(5)	0.4450(5)	−0.3230(7)	5.4(2)
C(56)	0.1465(4)	0.3867(4)	−0.2391(6)	4.6(1)
C(61)	−0.0480(3)	0.1391(3)	−0.2920(5)	3.0(1)
C(62)	−0.1104(4)	0.0786(4)	−0.2549(6)	4.6(1)
C(63)	−0.1709(5)	−0.0051(5)	−0.3469(7)	6.1(2)
C(64)	−0.1707(5)	−0.0271(5)	−0.4714(7)	5.6(2)

Table 3 (continued)

Atom	x	y	z	B (Å^2) [a]
C(65)	−0.1064(5)	0.0297(5)	−0.5072(8)	6.5(2)
C(66)	−0.0444(5)	0.1137(5)	−0.4176(7)	5.3(2)
C(71)	−0.0401(3)	0.2921(3)	−0.0993(5)	2.9(1)
C(72)	−0.1451(4)	0.2672(4)	−0.1622(6)	4.8(1)
C(73)	−0.1991(5)	0.3124(5)	−0.1090(7)	5.9(2)
C(74)	−0.1489(5)	0.3801(5)	0.0078(7)	5.2(1)
C(75)	−0.0463(5)	0.4052(5)	0.0715(7)	6.3(2)
C(76)	0.0090(5)	0.3596(5)	0.0170(7)	5.3(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)\ B(1,2)+ac(\cos\beta)\ B(1,3)+bc(\cos\alpha)\ B(2,3)]$. [b] Atoms C(21)–C(76) were refined isotropically.

to 3.2 Å^2 for the phenyl hydrogens and 2.8 Å^2 for the pyrazolyl hydrogens. Hydrogen atoms were allowed to "ride" on their attached carbon.

Refinement was carried out by full-matrix, for **3** and blocked-matrix least-squares techniques for **4** using the neutral atom scattering factors [20,21] and anomalous dispersion terms [22] obtained from the usual sources.

The positional and isotropic thermal parameters for the two structures are given in Tables 3 and 4. Structure amplitudes, anisotropic thermal parameters, hydrogen atom parameters, and parameters for the phenyl rings are available from M.C. upon request (Tables S1–S4 for compound **3**, S5–S8 for compound **4**).

Results and discussion

(a) Description of structures

(i) $[Ru_2(CO)_4(\mu\text{-}NC_5H_4O)_2(PPh_3)_2]$ (3). As shown in Fig. 1, this binuclear complex has the two ruthenium centers bridged, in a head-to-tail fashion, by the 2-oxypyridinate ligands. Each ruthenium has a distorted octahedral geometry in which the two oxypyridinate ligands, one binding through oxygen and the other through nitrogen, occupy mutually *cis* positions in the equatorial plane opposite the carbonyl ligands. The axial sites are occupied by the other Ru atom and the PPh_3 ligand. In this geometry the equatorial carbonyls have the "sawhorse" arrangement previously observed in $[Ru_2(CO)_6(\mu\text{-dmpz})_2]$ * [3], $[Ru_2(CO)_6(\mu\text{-}O_2CR)_2]$ [23], $[Ru_2(CO)_4(pyr)_2(\mu\text{-mbt})_2]$ * [15] and $[Ru_2(CO)_4(\mu\text{-}O_2CC_3H_7)_2(P^tBu_3)_2]$ [24]. The two dimetallooxypyridinate rings are almost orthogonal, having a dihedral angle of 84.2(1)°, comparing well with the value of 88.8° in the butyrate-bridged complex [24]. The geometry about each Ru atom is close to that expected for an octahedron with angles between adjacent groups ranging from 81.47(7)° to 98.43(9)°.

Distortions from the idealized 90° result because of the strain imposed by the bridging groups which, in this structure, have a bite distance of ca. 2.30 Å. Since this distance is appreciably less than the Ru–Ru separation of 2.7108(4) Å, the two Ru equatorial planes are inclined to each other by 16.2(4)°. A further indication of this

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* dmpz = dimethylpyrazolyl, mbt = mercaptobenzothiazolate

Table 4

Positional and isotropic thermal parameters for $[Ru(CO)_2(\mu\text{-}N_2C_3H_3)(PPh_3)]_2$ (4)

Atom	x	y	z	B (Å^2) [a]
Ru(1)	0.22375(3)	0.18328(3)	0.19211(2)	2.495(8)
Ru(2)	0.36378(3)	0.17573(3)	0.28585(2)	2.574(8)
N(11)	0.2901(3)	0.3128(3)	0.2028(2)	2.8(1)
N(12)	0.3611(4)	0.3078(3)	0.2477(2)	3.2(1)
N(21)	0.1506(3)	0.2108(3)	0.2780(2)	2.7(1)
N(22)	0.2200(3)	0.2073(3)	0.3248(2)	2.9(1)
C(11)	0.3023(5)	0.3907(4)	0.1728(3)	3.5(2)
C(12)	0.3807(5)	0.4382(4)	0.1980(3)	4.4(2)
C(13)	0.4170(5)	0.3826(4)	0.2456(3)	4.1(2)
C(21)	0.0609(4)	0.2290(4)	0.3044(3)	3.2(2)
C(22)	0.0697(5)	0.2358(4)	0.3675(3)	3.6(2)
C(23)	0.1710(4)	0.2229(4)	0.3789(3)	3.4(2)
C(1)	0.3115(4)	0.1590(4)	0.1263(3)	3.5(2)
C(2)	0.1939(5)	0.0615(4)	0.1962(3)	3.5(2)
C(3)	0.4746(5)	0.1488(4)	0.2359(3)	4.0(2)
C(4)	0.3494(5)	0.0522(4)	0.2986(3)	3.6(2)
O(1)	0.3653(4)	0.1431(3)	0.0855(2)	5.5(1)
O(2)	0.1807(3)	−0.0152(3)	0.1975(2)	4.9(1)
O(3)	0.5431(3)	0.1324(3)	0.2043(2)	5.8(1)
O(4)	0.3417(4)	−0.0241(3)	0.3017(2)	5.0(1)
P(1)	0.0775(1)	0.2208(1)	0.1293(1)	2.85(3)
C(111)	0.0151(4)	0.3298(4)	0.1405(3)	3.0(1)
C(112)	−0.0646(5)	0.3533(4)	0.1015(3)	4.1(2)
C(113)	−0.1146(5)	0.4351(5)	0.1107(3)	4.5(2)
C(114)	−0.0813(6)	0.4928(5)	0.1581(3)	4.6(2)
C(115)	−0.0020(5)	0.4705(4)	0.1954(3)	4.6(2)
C(116)	0.0457(5)	0.3866(4)	0.1879(3)	3.7(2)
C(121)	−0.0253(5)	0.1394(4)	0.1409(3)	3.2(2)
C(122)	−0.0130(5)	0.0520(4)	0.1223(3)	4.7(2)
C(123)	−0.0831(7)	−0.0120(5)	0.1350(4)	6.3(2)
C(124)	−0.1678(6)	0.0095(6)	0.1692(4)	6.2(2)
C(125)	−0.1840(5)	0.0947(6)	0.1887(3)	5.6(2)
C(126)	−0.1131(5)	0.1612(5)	0.1743(3)	4.0(2)
C(131)	0.0946(5)	0.2221(4)	0.0438(3)	3.5(2)
C(132)	0.1805(5)	0.2659(5)	0.0219(3)	4.4(2)
C(133)	0.1959(6)	0.2733(5)	−0.0423(3)	6.6(2)
C(134)	0.1280(8)	0.2351(6)	−0.0830(4)	7.7(2)
C(135)	0.0424(6)	0.1931(6)	−0.0622(3)	6.7(2)
C(136)	0.0260(5)	0.1863(5)	0.0021(3)	5.1(2)
P(2)	0.4522(1)	0.2036(1)	0.3834(1)	3.10(3)
C(211)	0.4600(4)	0.3194(4)	0.4127(2)	3.2(2)
C(212)	0.5352(6)	0.3453(5)	0.4534(3)	4.9(2)
C(213)	0.5338(5)	0.4310(5)	0.4797(4)	6.2(2)
C(214)	0.4603(6)	0.4909(5)	0.4644(4)	5.5(2)
C(215)	0.3859(6)	0.4670(5)	0.4240(3)	5.0(2)
C(216)	0.3829(5)	0.3787(4)	0.3979(3)	4.2(2)
C(221)	0.3936(5)	0.1451(4)	0.4495(3)	3.4(2)
C(222)	0.3595(5)	0.1910(5)	0.5027(3)	4.0(2)
C(223)	0.3090(5)	0.1456(3)	0.5495(3)	4.7(2)
C(224)	0.2908(6)	0.0538(5)	0.5439(3)	5.1(2)
C(225)	0.3263(5)	0.0090(5)	0.4934(3)	4.9(2)
C(226)	0.3772(5)	0.0527(4)	0.4463(3)	4.2(2)
C(231)	0.5851(5)	0.1659(5)	0.3871(3)	4.2(2)

Table 4 (continued)

Atom	x	y	z	B (Å^2) [a]
C(232)	0.6495(5)	0.1984(5)	0.3409(3)	5.5(2)
C(233)	0.7529(6)	0.1703(8)	0.3452(4)	8.1(2)
C(234)	0.7865(8)	0.1159(7)	0.3907(5)	9.3(4)
C(235)	0.7217(7)	0.0859(7)	0.4357(5)	8.6(2)
C(236)	0.6220(6)	0.1109(5)	0.4340(4)	5.8(2)

[a] Equivalent isotropic B as defined in Table 3.

tilt in the equatorial planes is given by the acute Ru–Ru–X angles (X = N or O of the bridging oxypyridinate groups) of between 81.47(7)° and 82.98(9)°. The Ru–Ru separation is normal for a single bond and can be compared to values ranging from 2.639(1) to 2.759(4) Å in analogous dimers [3,4,23,24]. In order to minimize the close non-bonded contacts between the equatorial ligands on the two metals, brought about by the metal–metal bonding, the two octahedra are twisted by approximately 22° about the Ru–Ru bond.

The distances involving all the carbonyl groups are normal and do not differ significantly in spite of two different environments (*trans* to O or N). Similarly the Ru–O and Ru–N distances involving the oxypyridinate groups are normal, comparing well with analogous distances in carboxylate [23,24] and mercaptobenzothiazolato-bridged [15] species. Both Ru–P distances (2.440(1), 2.450(1) Å) are normal, but do appear to be somewhat longer than frequently observed [25–27] in triphenylphosphine complexes of Ru in which values near 2.35 Å seem typical, and are longer than those observed (av. 2.373(2) Å) in the analogous dppm-bridged * Ru^I complex, $[Ru_2(CO)_4(\mu\text{-}O_2CCH_3)(dppm)_2]^+$, in which the phosphines occupy the equatorial positions *cis* to the Ru–Ru bond [4]. It appears that the lengthening of these bonds in **3** results from the high *trans* influence of the metal–metal bond as seen

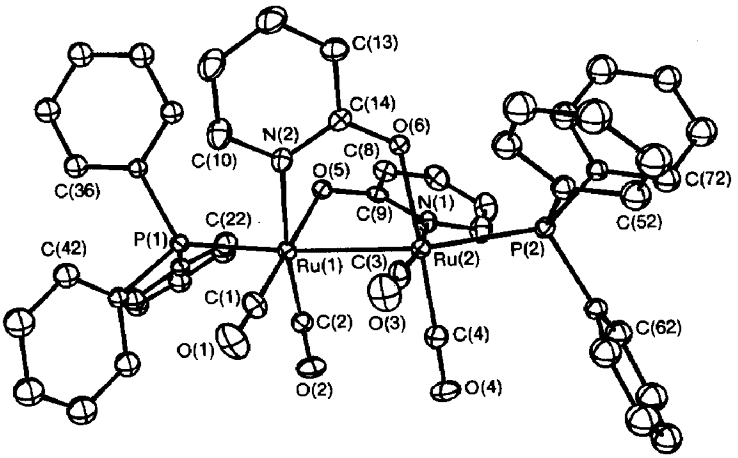

Fig. 1. A perspective view of $[Ru_2(CO)_4(\mu\text{-}NC_5H_4O)_2(PPh_3)_2]$ (**3**) showing the numbering scheme. Thermal ellipsoids are shown at the 20% level. Hydrogens are omitted.

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* dppm = bis(diphenylphosphino)methane.

Table 5

Bond lengths (Å) for $[Ru_2(CO)_2(\mu\text{-}NC_5H_4O)(PPh_3)]_2$ [a] (3)

Ru(1)-Ru(2) [b]	2.7108(4)	O(2)-C(2)	1.168(5)
Ru(1)-P(1)	2.440(1)	O(3)-C(3)	1.156(5)
Ru(1)-O(5)	2.104(3)	O(4)-C(4)	1.150(6)
Ru(1)-N(2)	2.175(3)	O(5)-C(9)	1.292(5)
Ru(1)-C(1)	1.829(5)	O(6)-C(14)	1.288(5)
Ru(1)-C(2)	1.839(5)	N(1)-C(5)	1.365(5)
Ru(2)-P(2)	2.450(1)	N(1)-C(9)	1.357(5)
Ru(2)-O(6)	2.112(3)	N(2)-C(10)	1.379(6)
Ru(2)-N(1)	2.166(3)	N(2)-C(14)	1.358(5)
Ru(2)-C(3)	1.847(5)	C(5)-C(6)	1.373(7)
Ru(2)-C(4)	1.841(5)	C(6)-C(7)	1.391(8)
P(1)-C(21)	1.836(4)	C(7)-C(8)	1.343(7)
P(1)-C(31)	1.827(4)	C(8)-C(9)	1.417(6)
P(1)-C(41)	1.827(4)	C(10)-C(11)	1.375(7)
P(2)-C(51)	1.839(5)	C(11)-C(12)	1.393(8)
P(2)-C(61)	1.832(4)	C(12)-C(13)	1.360(7)
P(2)-C(71)	1.825(4)	C(13)-C(14)	1.399(6)
O(1)-C(1)	1.155(5)		

[a] Parameters for the phenyl rings are given in the Supplementary Material, Table S4. [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

previously for σ-donor ligands [28]. Certainly previous reports [2,29,30] on related acetate-bridged Ru^I dimers indicate that the axial ligands are labile. In compound 3 the PPh_3 ligands deviate only ca. 10° from the Ru–Ru axis with Ru–Ru–P angles of 170.32(3)° and 170.79(3)°.

The C–N distances within the oxypyridinate rings range from 1.357(5) to 1.379(5) Å and appear to be normal [31]. Similarly the C–O distances involving these ligands (1.292(5), 1.288(5) Å) do not appear unusual, although they are somewhat short suggesting some multiple bond character [31]. Relevant bond lengths and selected bond angles for complex 3 are listed in Tables 5 and 6.

(ii) $[Ru_2(CO)_4(\mu\text{-}N_2C_3H_3)_2(PPh_3)_2]$ *(4).* This structure, shown in Fig. 2, very closely resembles that of the oxypyridinate-bridged analogue (3), having the two pyrazolate ligands mutually *cis*, the carbonyls opposite the pyrazolate groups in a sawhorse arrangement, and the phosphines in axial sites opposite the Ru–Ru bond. Subtle differences in the two structures seem to originate from the smaller bite of the pyrazolate ligand, with an N–N separation (ca. 1.35 Å) which is ca. 1 Å less than the O...N separation in the oxypyridinate ligand. As a result the angles at the Ru centers involving mutually *cis* ligands display a wider spread (70.6(1)°–100.4(1)°) about the idealized 90°, with the acute angles involving the bridging groups. In addition, the dihedral angle between the two Ru equatorial planes (35.4(1)°) is greater than in the oxypyridinate-bridged compound 3. This greater tilt in compound 4 is mirrored by the greater deviations of the phosphines from the axial positions (Ru–Ru–P angles 161.9(1)°, 163.5(1)°). As a further indication of the strain imposed by the bridging ligands, the Ru–N–N angles (108.3(3)–109.8(3)°) deviate considerably from the expected 120° [32]. The dihedral angle between the two pyrazolate rings, at 75°, is much less than the values noted earlier for compound 3 and bisacetate-bridged species [24]; this may also be a consequence of the strain imposed by the smaller bite of the pyrazolate groups.

Table 6

Selected Angles (deg) for $[Ru(CO)_2(\mu\text{-}NC_5H_4O)(PPh_3)]_2$ (3)

(a) Bond angles					
Ru(2)-Ru(1)-P(1)	170.32(3)	N(1)-Ru(2)-C(3)	171.3(2)	N(1)-C(5)-C(6)	123.8(5)
Ru(2)-Ru(1)-O(5)	81.53(7)	N(1)-Ru(2)-C(4)	92.0(2)	C(5)-C(6)-C(7)	117.8(5)
Ru(2)-Ru(1)-N(2)	82.43(9)	C(3)-Ru(2)-C(4)	89.1(2)	C(6)-C(7)-C(8)	119.9(5)
Ru(2)-Ru(1)-C(1)	96.9(1)	Ru(1)-P(1)-C(21)	116.0(1)	C(7)-C(8)-C(9)	120.7(5)
Ru(2)-Ru(1)-C(2)	90.3(1)	Ru(1)-P(1)-C(31)	121.5(1)	O(5)-C(9)-N(1)	120.9(4)
P(1)-Ru(1)-O(5)	88.95(8)	Ru(1)-P(1)-C(41)	110.1(1)	O(5)-C(9)-C(8)	119.0(4)
P(1)-Ru(1)-N(2)	98.43(9)	C(21)-P(1)-C(31)	98.2(2)	N(1)-C(9)-C(8)	120.1(4)
P(1)-Ru(1)-C(1)	92.7(1)	C(21)-P(1)-C(41)	104.1(2)	N(2)-C(10)-C(11)	122.9(5)
P(1)-Ru(1)-C(2)	88.7(1)	C(31)-P(1)-C(41)	105.1(2)	C(10)-C(11)-C(12)	119.3(5)
O(5)-Ru(1)-N(2)	84.5(1)	Ru(2)-P(2)-C(51)	113.3(1)	C(11)-C(12)-C(13)	117.7(5)
O(5)-Ru(1)-C(1)	176.0(2)	Ru(2)-P(2)-C(61)	111.1(1)	C(12)-C(13)-C(14)	122.3(5)
O(5)-Ru(1)-C(2)	94.2(2)	Ru(2)-P(2)-C(71)	122.7(1)	O(6)-C(14)-N(2)	120.0(4)
N(2)-Ru(1)-C(1)	91.6(2)	C(51)-P(2)-C(61)	103.5(2)	O(6)-C(14)-C(13)	120.1(4)
N(2)-Ru(1)-C(2)	172.7(2)	C(51)-P(2)-C(71)	99.3(2)	N(2)-C(14)-C(13)	119.9(4)
C(1)-Ru(1)-C(2)	89.5(2)	C(61)-P(2)-C(71)	105.1(2)	P(1)-C(21)-C(22)	116.2(3)
Ru(1)-Ru(2)-P(2)	170.79(3)	Ru(1)-O(5)-C(9)	123.6(2)	P(1)-C(21)-C(26)	123.5(3)
Ru(1)-Ru(2)-O(6)	81.47(7)	Ru(2)-O(6)-C(14)	124.7(3)	P(1)-C(31)-C(32)	119.3(3)
Ru(1)-Ru(2)-N(1)	82.98(9)	Ru(2)-N(1)-C(5)	123.5(3)	P(1)-C(31)-C(36)	121.5(3)
Ru(1)-Ru(2)-C(3)	88.3(1)	Ru(2)-N(1)-C(9)	118.9(3)	P(1)-C(41)-C(42)	121.8(3)
Ru(1)-Ru(2)-C(4)	95.9(1)	C(5)-N(1)-C(9)	117.5(4)	P(1)-C(41)-C(46)	118.7(3)
P(2)-Ru(2)-O(6)	89.51(8)	Ru(1)-N(2)-C(10)	123.3(3)	P(2)-C(51)-C(52)	122.0(4)
P(2)-Ru(2)-N(1)	97.95(9)	Ru(1)-N(2)-C(14)	118.7(3)	P(2)-C(51)-C(56)	119.9(4)
P(2)-Ru(2)-C(3)	90.6(1)	C(10)-N(2)-C(14)	117.5(4)	P(2)-C(61)-C(62)	120.5(4)
P(2)-Ru(2)-C(4)	93.3(1)	Ru(1)-C(1)-O(1)	178.8(5)	P(2)-C(61)-C(66)	121.0(4)
O(6)-Ru(2)-N(1)	83.9(1)	Ru(1)-C(2)-O(2)	178.1(4)	P(2)-C(71)-C(72)	124.1(4)
O(6)-Ru(2)-C(3)	94.7(2)	Ru(2)-C(3)-O(3)	179.8(8)	P(2)-C(71)-C(76)	117.2(4)
O(6)-Ru(2)-C(4)	175.4(2)	Ru(2)-C(4)-O(4)	179.7(6)		
(b) Torsion angles					
O(5)-Ru(1)-Ru(2)-N(1)	-23.5(2)	C(1)-Ru(1)-Ru(2)-C(3)	-19.9(3)		
N(2)-Ru(1)-Ru(2)-O(6)	-24.2(1)	C(2)-Ru(1)-Ru(2)-C(4)	-20.6(3)		

The Ru-Ru separation of 2.732(1) Å is somewhat longer than that observed in 3 possibly because of the above-noted strain, and is shorter than the distance (2.759(4) Å [15]) observed in the mercaptobenzothiazolato-bridged species in which it appears

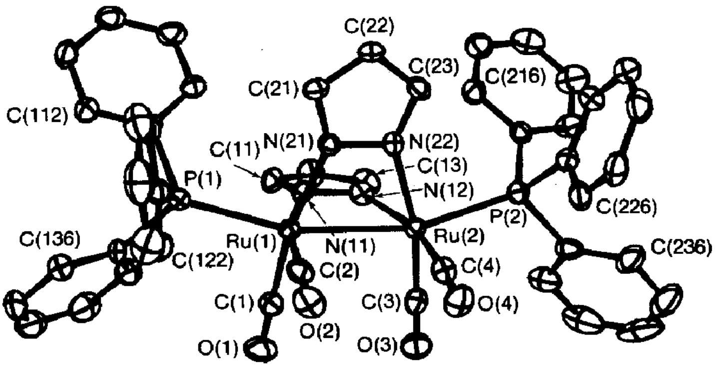


Fig. 2. A perspective view of $[Ru_2(CO)_4(\mu\text{-}N_2C_3H_3)_2(PPh_3)_2]$ (4) together with the numbering scheme. 30% thermal ellipsoids are shown.

Table 7

Bond lengths (Å) for $[Ru(CO)_2(\mu\text{-}N_2C_3H_3)(PPh_3)]_2$ (4)

Ru(1)–Ru(2)	2.732(1)	N(22)–C(23)	1.346(7)
Ru(1)–N(11)	2.126(5)	C(11)–C(12)	1.366(9)
Ru(1)–N(21)	2.116(4)	C(12)–C(13)	1.396(9)
Ru(1)–C(1)	1.860(6)	C(21)–C(22)	1.359(8)
Ru(1)–C(2)	1.852(6)	C(22)–C(23)	1.374(8)
Ru(1)–P(1)	2.420(2)	C(1)–O(1)	1.151(7)
Ru(2)–N(12)	2.124(4)	C(2)–O(2)	1.153(7)
Ru(2)–N(22)	2.128(4)	C(3)–O(3)	1.155(8)
Ru(2)–C(3)	1.858(6)	C(4)–O(4)	1.140(7)
Ru(2)–C(4)	1.863(6)	P(1)–C(111)	1.832(6)
Ru(2)–P(2)	2.428(2)	P(1)–C(121)	1.835(6)
N(11)–N(12)	1.346(6)	P(1)–C(131)	1.844(6)
N(11)–C(11)	1.331(7)	P(2)–C(211)	1.832(6)
N(12)–C(13)	1.335(8)	P(2)–C(221)	1.832(6)
N(21)–N(22)	1.360(6)	P(2)–C(231)	1.847(6)
N(21)–C(21)	1.341(7)		

Table 8

Selected Angles (deg) for $[Ru(CO)_2(\mu\text{-}N_2C_3H_3)(PPh_3)]_2$ (4).

Bond angles

Ru(2)–Ru(1)–N(11)	71.3(1)	N(12)–Ru(2)–P(2)	100.4(1)	Ru(2)–C(4)–O(4)	174.9(5)
Ru(2)–Ru(1)–N(21)	71.3(1)	N(22)–Ru(2)–P(2)	93.2(1)	Ru(1)–P(1)–C(111)	119.3(2)
N(11)–Ru(1)–N(21)	85.5(2)	C(3)–Ru(2)–P(2)	98.8(2)	Ru(1)–P(1)–C(121)	111.4(2)
Ru(2)–Ru(1)–C(1)	97.2(2)	C(4)–Ru(2)–P(2)	95.2(2)	C(111)–P(1)–C(121)	103.4(3)
N(11)–Ru(1)–C(1)	90.0(2)	Ru(1)–N(11)–N(12)	108.3(3)	Ru(1)–P(1)–C(131)	117.1(2)
N(21)–Ru(1)–C(1)	168.5(2)	Ru(1)–N(11)–C(11)	141.6(4)	C(111)–P(1)–C(131)	100.1(3)
Ru(2)–Ru(1)–C(2)	94.0(2)	N(12)–N(11)–C(11)	107.9(4)	C(121)–P(1)–C(131)	103.4(3)
N(11)–Ru(1)–C(2)	165.0(2)	Ru(2)–N(12)–N(11)	109.8(3)	P(1)–C(111)–C(112)	119.0(4)
N(21)–Ru(1)–C(2)	92.9(2)	Ru(2)–N(12)–C(13)	140.5(4)	P(1)–C(111)–C(116)	120.3(4)
C(1)–Ru(1)–C(2)	88.8(3)	N(11)–N(12)–C(13)	108.4(4)	P(1)–C(121)–C(122)	119.8(5)
Ru(2)–Ru(1)–P(1)	163.5(1)	Ru(1)–N(21)–N(22)	108.9(3)	P(1)–C(121)–C(126)	122.0(5)
N(11)–Ru(1)–P(1)	100.4(1)	Ru(1)–N(21)–C(21)	144.0(4)	P(1)–C(131)–C(132)	116.1(4)
N(21)–Ru(1)–P(1)	94.2(1)	N(22)–N(21)–C(21)	107.0(4)	P(1)–C(131)–C(136)	123.9(5)
C(1)–Ru(1)–P(1)	97.0(2)	Ru(2)–N(22)–N(21)	108.8(3)	Ru(2)–P(2)–C(211)	118.8(2)
C(2)–Ru(1)–P(1)	94.6(2)	Ru(2)–N(22)–C(23)	143.6(4)	Ru(2)–P(2)–C(221)	112.4(2)
Ru(1)–Ru(2)–N(12)	70.6(1)	N(21)–N(22)–C(23)	107.6(4)	C(211)–P(2)–C(221)	101.8(3)
Ru(1)–Ru(2)–N(22)	70.9(1)	N(11)–C(11)–C(12)	110.5(5)	Ru(2)–P(2)–C(231)	116.3(2)
N(12)–Ru(2)–N(22)	86.1(2)	C(11)–C(12)–C(13)	104.1(5)	C(211)–P(2)–C(231)	102.5(3)
Ru(1)–Ru(2)–C(3)	96.9(2)	N(12)–C(13)–C(12)	109.0(5)	C(221)–P(2)–C(231)	103.0(3)
N(12)–Ru(2)–C(3)	89.5(2)	N(21)–C(21)–C(22)	111.0(5)	P(2)–C(211)–C(212)	121.3(5)
N(22)–Ru(2)–C(3)	167.9(2)	C(21)–C(22)–C(23)	104.4(5)	P(2)–C(211)–C(216)	118.5(4)
Ru(1)–Ru(2)–C(4)	94.5(2)	N(22)–C(23)–C(22)	109.9(5)	P(2)–C(221)–C(222)	122.2(5)
N(12)–Ru(2)–C(4)	164.3(2)	Ru(1)–C(1)–O(1)	179.3(5)	P(2)–C(221)–C(226)	119.7(5)
N(22)–Ru(2)–C(4)	93.9(2)	Ru(1)–C(2)–O(2)	176.1(5)	P(2)–C(231)–C(232)	116.5(5)
C(3)–Ru(2)–C(4)	87.3(3)	Ru(2)–C(3)–O(3)	179.3(6)	P(2)–C(231)–C(236)	123.2(5)
Ru(1)–Ru(2)–P(2)	161.9(1)				

Torsion angles

N(11)–Ru(1)–Ru(2)–N(12)	−1.2(2)	C(1)–Ru(1)–Ru(2)–C(3)	0.7(3)
N(21)–Ru(1)–Ru(2)–N(22)	−0.1(2)	C(2)–Ru(1)–Ru(2)–C(4)	0.8(3)

that the metal–metal separation is lengthened by the large bite of this group. However, this separation in **4** is also longer than in the 3,5-dimethylpyrazolate-bridged complex (2.705(2) Å) [3], a result which is unexpected based on the near equivalence of the two bridging groups. It may be that the different axial groups (PPh_3 vs. CO) are responsible for this difference. In contrast, the non-ruthenium–ruthenium bonded pyrazolate bridged complexes, $[(Ru(\mu\text{-Pz})(PzH)(COD))_2(\mu\text{-H})]PF_6$ and $[Ru_2(\mu\text{-Pz})_2(Cl)(PzH)(COD)_2(\mu\text{-H})] \cdot C_2H_5OH$ [33] have much larger Ru–Ru separations of 3.105(1) and 3.112(1) Å, respectively, representing a more open $Ru_2(\mu\text{-Pz})_2$ unit. Again in compound **4** the Ru–P distances (2.420(2), 2.428(2) Å) are somewhat longer than normal, in accordance with the lengthening of $M\text{–}X_{ax}$ bonds in metal-metal bonded complexes. Relevant bond lengths and selected bond angles for complex **4** are listed in Tables 7 and 8.

(b) Description of chemistry

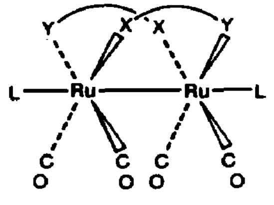
The carboxylate-bridged complexes $[Ru_2(CO)_4(\mu\text{-}O_2CCH_3)_2L_2]$ (L = NCMe (**1a**), PPh_3 (**1b**)), which are readily prepared from the polymeric $[Ru_2(CO)_4(\mu\text{-}O_2CCH_3)_2]_n$ [2], are shown to be convenient synthons for a series of anion-bridged, binuclear complexes of Ru^I. Two of these new species, $[Ru_2(CO)_4(\mu\text{-XY})_2(PPh_3)_2]$ ($XY^- = NC_3H_4S_2^-$ (**2**), $NC_5H_4O^-$ (**3**)) are readily prepared by reaction of **1b** with the appropriate sodium salts as outlined in eqn. 1, and are obtained in essentially quantitative conversions based on ^{31}P NMR spectroscopy. Although $[Ru_2(CO)_4(\mu\text{-Pz})_2(PPh_3)_2]$ (**4**) could not be obtained pure by this route it was synthesized by a

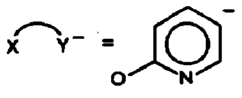
$$[Ru_2(CO)_4(\mu-O_2CCH_3)_2(PPh_3)_2] \xrightarrow{NaXY} [Ru_2(CO)_4(\mu-XY)_2(PPh_3)_2] + 2NaO_2CCH_3 \quad (1)$$

closely related route involving the reaction of **1a** with two equivalents of sodium pyrazolate and PPh_3 in refluxing methanol. This latter route suggests that a large variety of related complexes will be accessible through replacement of the acetate anions by other anionic ligands and by displacement of the labile acetonitrile ligands by other neutral 2-electron donor ligands such as CO, amines, phosphines or related species. Although this is in principle another route to the hexacarbonyl, pyrazolate-bridged complexes of Oro [3], we have not yet tested this hypothesis.

Compound **4** was also obtained as an unexpected product from the reaction of the polymeric $[Ru_2(CO)_4(O_2CCH_3)_2]_n$ with $NaEt_2B(Pz)_2$ and PPh_3 in refluxing methanol, although it is not clear how the fragmentation of the pyrazolylborate ligand occurred to yield this product.

The compounds synthesized have the sawhorse structure diagrammed below, in which the two carbonyl ligands on each metal are mutually *cis* and opposite the bridging groups, with the phosphine ligands in the axial sites opposite the Ru–Ru bond. As such these structures very much resemble analogues of the acetate-bridged





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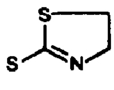

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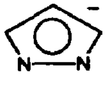

4

precursors [23,24]. The IR spectra in the carbonyl region of these C_{2v} sawhorse structures are rather distinctive [34], showing the characteristic alternating strong-medium-strong-weak intensity pattern (see Table 1), and can be contrasted to the known cases in which a pair of the equatorial carbonyls have rearranged to the axial positions opposite the Ru–Ru bond [4,15] where a medium-strong-strong-weak pattern results in the IR spectra.

Although the three bridging groups in compounds **2**–**4** superficially resemble each other, there are two important distinctions. First, the pyrazolate group (like the carboxylates) binds both metals by the same atom type, whereas the 2-oxypyridinate and the 2-mercaptothiazolinate groups bind through different atom types. It is of interest to compare the chemistry of these types, particularly with ligands having one hard (O, N) and one soft (S) donor atom since each end of the ligand will presumably display differing labilities. Second, the pyrazolate bridge has two atoms bridging the metals whereas the others have three atoms in the bridge. We have already seen, in the structures of **3** and **4**, that the two-atom bridge induces significantly more strain in the complex and the effects of this strain on the reactivity are being investigated. An obvious extention of this study, to investigate binuclear Ru^I complexes bridged by single-atom bridges, such as phosphide (PR_2^-), thiolate (SR^-), alkoxide (OR^-) and other pseudo halides, is also underway. We anticipate that the convenient routes, described herein, for the preparation of binuclear Ru^I complexes will prove to be much more general and will lead to a wide range of related species.

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