

High-pressure synthesis of $[Ru_2(\mu-dppm)_2 (\mu-CO)(CO)_4, Ru_2(\mu-dppm)(\mu-dmpm) (\mu-CO)(CO)_4]$, and $[Ru(dcypm)(CO)_3]$ from Ru_3(CO)_{12} and the diphosphines : R_2PCH_2PR_2; R = CH_3(dmpm), C_6H_5 (dppm) and C_6H_{11} (dcypm). Crystal and molecular structures of $[Ru_2(\mu-dppm)_2(\mu-CO)(CO)_4]$, and $[Ru(dcypm)(CO)_3]$

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Abstract—The high-pressure (1300 psi CO, 120°C) reactions of $Ru_3(CO)_{12}$ with the diphosphines $R_2PCH_2PR_2$; $R = CH_3$ (dmpm), C_6H_5 (dppm), and C_6H_{11} (dcypm), are reported. In the case of dppm, the disphosphinebridged dinuclear ruthenium complex $[Ru_2(\mu$ -dppm)_2(μ -CO)(CO)_4] was obtained. The corresponding reaction with dcypm afforded the mononuclear chelated diphosphine complex $[Ru(dcypm)(CO)_3]$. The mixed ligand system $[Ru_2(\mu$ -dppm)(μ -dmpm)(μ -CO)(CO)_4] was obtained by employing a 1:1 mixture of dppm and dmpm. The crystal and molecular structures of $[Ru_2(\mu$ -dppm)_2(μ -CO)(CO)_4] and $[Ru(dcypm)(CO)_3]$ were also determined. (© 1997 Elsevier Science Ltd. All rights reserved.

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Diphosphine and diphosphazane-bridged dinuclear ruthenium complexes have been the subject of considerable study [1–10]. The chemistry of dinuclear ruthenium diphosphazane complexes, $1 (R = Me, tPr^{i}$ or Ph), has been pursued extensively in the laboratories of Haines and co-workers [1–6]. The study of these complexes has led to a detailed model system for the stepwise oxidation of CO to CO₂ [6] as well as to a novel photochemical Michaelis–Arbuzov-type rearrangement [11]. We have therefore sought to expand the scope of this class of dinuclear transition metal complexes.

The high-pressure synthesis of the bis(dimethylphosphino)methane (dmpm)-bridged complex **2** was reported by Johnson and Gladfelter [7]. The bis(diphenylphosphino)methane (dppm)-bridged complex $[Ru_2(\mu$ -dppm)_2(μ -CO)(CO)_4] (**3**) was first synthesized by the photochemical reaction of $Ru_3(CO)_{12}$ with dppm [8]. More recently, **3** was also prepared by the reduction of ruthenium acetate in the presence of carbon monoxide, although the structure of this material has yet to be reported [9]. We report studies of the high-pressure (1300 psi CO, 120°C) reactions of $Ru_3(CO)_{12}$ with the diphosphines $R_2PCH_2PR_2$; $R = CH_3$ (dmpm), C_6H_5 (dppm) and C_6H_{11} (dcypm), including the preparation of the mixed-ligand system

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 $[Ru_2(\mu-dppm)(\mu-dmpm)(\mu-CO)(CO)_4]$ (4) and the mononuclear complex $[Ru(dcypm)(CO)_3]$ (5). The crystal and molecular structures of 3 and 5 are also described.

EXPERIMENTAL

All manipulations were carried out under nitrogen in a VAC glove-box, or using standard Schlenk techniques. Toluene was distilled from sodium prior to use. Hexane was used as purchased from Fisher Scientific. Ru₃(CO)₁₂ and dmpm [bis(dimethyl-phosphino) methane] were purchased from Strem. Dppm [bis (dimethylphosphino)methane] was purchased from Aldrich. Dcypm [bis(dicyclohexylphosphino)methane] was obtained from Dr. I. P. Rothwell (Purdue University). The complex $[Ru_2(\mu-dmpm)_2(\mu-CO)(CO)_4]$ was prepared according to the literature procedure [7]. IR spectra of compounds as KBr pellets were recorded using a Perkin-Elmer 1710 Fourier transform infrared spectrometer. ¹H and ³¹P-[¹H] NMR spectra were recorded on either Varian XL-200 or General Electric 300 spectrometers.

Preparation of $[Ru_2(\mu-dppm)_2(\mu-CO)(CO)_4]$ (3)

Complex 3 was prepared by a modification of Gladfelter's method [7] for the synthesis of $[Ru_2(\mu-dmpm)_2 (\mu-CO(CO)_4]$. $Ru_3(CO)_{12}$ (0.940 g, 1.47 mmol) and dppm (1.697 g, 4.41 mmol) were placed in a 500 cm^3 high-pressure Parr reactor to which 100 cm³ of toluene was added. The reactor was charged and sealed in the dry-box and then placed in a heating well and pressurized with CO to ca 1000 psi. Upon heating to 120°C, the reactor pressure rose to ca 1300 psi. The reaction was stirred under these conditions using a mechanical stirrer for 16 h, after which it was cooled to room temperature and vented. The reactor was then returned to the dry-box where the reaction contents were transferred to a round-bottomed flask and reduced in volume under vacuum to $ca 50 \text{ cm}^3$ and precipitated with ca 200 cm³ hexane. A yellow solid was recovered by filtration, rinsed with hexane and dried in vacuo. Yield: 2.06 g (84%). ¹H NMR (200 MHz, C_6D_6): δ_H 3.4 (4H, m, CH₂), 6.7–7.7 (40H, m, CH). ³¹P-[¹H] NMR (81 MHz, C_6D_6) : δ_P 39.9 (s). IR (KBr) v(CO) cm⁻¹: 1964 s, 1918 vs, 1894 vs, 1872 s, 1700 s.

Preparation of $[Ru_2(\mu-dppm)(\mu-dmpm)(\mu-CO)(CO)_4]$ (4)

Complex 4 was prepared by a similar method to that for 3 but equimolar amounts of dppm and dmpm were used; $Ru_3(CO)_{12}$ (470 g, 736 mmol), dmpm (0.18 cm³, 1.1 mmol) and dppm (425 g, 1.11 mmol). The final reaction mixture contained essentially a statistical mixture of 4, 3 and $[Ru_2(dmpm)_2(CO)_5]$.

Reducing the solution volume to *ca* 30 cm³ resulted in precipitation of $[Ru_2(dmpm)_2(CO)_5]$. This was removed by filtration and then through successive addition of hexane and filtration, **4** and then **3** were isolated and dried *in vacuo*. For **4**: Yield: 0.33 g (30%). ³¹P-{¹H} NMR (81 MHz, C₆D₆(: δ (AA'BB') 15.3 (m), 39.4 (m). IR (KBr)v(CO) cm⁻¹: 1951 s, 1912 vs, 1895 vs, 1867 s, 1682 s.

Preparation of [Ru(dcypm)(CO)₃] (5)

Complex 5 was prepared by a similar method to that for 3, but dcypm was substituted for dppm; Ru₃(CO)₁₂ (266 mg, 416 mmol) and dcypm (510 mg, 1.25 mmol). Light yellow needles of 5 crystallized upon reducing solvent volume. For 5: ¹H NMR (200 MHz, C₆D₆): $\delta_{\rm H}$ 2.7 (2H, t, CH₂), 1.0–2.1 (44H, broad overlapping m, cyclohex). ³¹P-{¹H} NMR (81 MHz, C₆H₆): δ_p – 3.30 (s) ppm. IR (KBr) v(CO) cm⁻¹: 1981 vs, 1899 vs, 1880 vs.

Crystal data for $[Ru_2(\mu-dppm)_2(\mu-CO)(CO)_4]$ (3)

X-ray quality crystals of 3.2CH₃CN, (C₅₉H₅₀N₂ $O_5P_4Ru_2$), were grown by slow evaporation from CH₃CN. An orange plate having approximate dimensions of $0.24 \times 0.20 \times 0.13$ mm³ was mounted in a glass capillary. Data collection were performed at 293 ± 1 K with Cu- K_x radiation ($\lambda = 1.54184$ Å) on an Enraf-Nonius CAD4 computer-controlled kappa-axis diffractometer equipped with a graphite crystal, incident beam monochromator. The crystal data and data collection parameters are given in Table 1. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $24 < \theta < 47^\circ$, measured by the computer-controlled diagonal slit method of centring. As a check on the crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.40° with a take-off angle of 6.0° , indicating good crystal quality. Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 63.8 cm⁻¹ for Cu- K_{α} radiation. An empirical absorption correction based on the method of Walker and Stuart was applied [12]. Relative transmission coefficients ranged from 0.478 to 1.000 with an average value of 0.639. The structure was solved using the structure solution program SHELX-86 [13]. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w (|F_{o}| - |F_{c}|)^{2}$ and the weight w is defined as by the Killean and Lawrence method with terms of 0.020 and 1.0 [14]. Scattering factors were taken from Cromer and Waber [15]. Anomalous dispersion effects were included in F_c [16]; the values for f' and f'' were those of Cromer [17]. All calculations were performed on a VAX computer. Refinement was done using MolEN [18]. Crystallographic drawings were done using programs ORTEP [19].

Crystal data for [Ru(dcypm)(CO)₃] (5)

X-ray quality crystals of 5, $(C_{28}H_{46}O_3P_2Ru)$, were grown by solvent evaporation from toluene. A colourless needle having approximate dimensions of $0.50 \times 0.35 \times 0.25$ mm³ was mounted in a glass capillary. The crystal data and data collection parameters are given in Table 1. Structural analysis was similar to that described for 3 with the following modifications. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $17 < \theta < 21^\circ$, measured by the computercontrolled diagonal slit method of centring. As a check on the crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.43° with a take-off angle of 3.0° , indicating good crystal quality. The structure was solved using the Patterson heavy-atom method which revealed the position of the Ru atom.

RESULTS AND DISCUSSION

The reaction of $[Ru_3CO_{12}]$ with dppm under 1000 psi CO in toluene led to the formation of $[Ru_2(\mu-dppm)_2(\mu-CO)(CO)_4]$ (3). In the presence of a 1:1 mixture of dppm and dmpm the mixed-ligand system $[Ru_2(\mu-dmpm)(\mu-dppm)(\mu-CO)(CO)_4]$ (4) was formed in essentially a statistical yield, along with 2 and 3. Complex 4 was isolated by fractional crystallization from toluene/hexane solutions. Upon continued addition of hexane, complex 2 crystallizes first, followed by 4 and then 3.

Table 2 compares the carbonyl infrared stretching frequencies of complexes 2–4 and the related diphosphazanes. As expected, increasing the basicity of the ligand from phosphazane to phosphine leads to a decrease in carbonyl stretching frequencies owing to increased π backbonding. Similarly, the less basic 3 shows higher stretching frequencies than 2. The mixed ligand system 4 exhibits v(CO) bands at frequencies that are intermediate between the bis(dmpm) and bis(dppm) compounds, 2 and 3. Complex 3, like 2, shows a singlet in the ³¹P NMR spectrum while the mixed-ligand system, 4, shows an AA'BB' pattern owing to the different phosphorus chemical environments of dmpm and dppm.

An ORTEP view of $[Ru_2(\mu-dppm)_2(\mu-CO)(CO)_4]$ (3) is shown in Fig. 1, and crystal data and data collection parameters are summarized in Table 1. Selected bond distances and angles are given in Table 3. the structure consists of two five-coordinate ruthenium centres separated by a Ru—Ru distance of

Table 1. Crystal data and data collection parameters

Compound	3 · 2CH ₃ CN	5
Formula	$C_{59}H_{50}N_2O_5P_{84}Ru_2$	$C_{28}H_{46}O_3P_2Ru$
Formula weight	1193.10	596.70
Space group	$P2_{1,n}$ (No. 14)	<i>P</i> 2 _{1/c} (No. 14)
a, Å	12.3250(9)	10.176(1)
b, Å	19.690(3)	21.649(3)
c, Å	22.1109(9)	14.261(3)
β,	103.1(3)	106.74(1)
$V, Å^3$	5226(7)	3008(2)
Ζ	4	4
$d_{\rm calc}, {\rm g}~{\rm cm}^{-3}$	1.516	1.311
Crystal dimensions, mm	$0.24 \times 0.20 \times 0.13$	$0.50 \times 0.35 \times 0.25$
Temperature, K	293	293
Radiation (wavelength)	$Cu-K_{\alpha}$ (1.54184 Å)	$Mo-K_{x}$ (0.71073 Å)
Monochromator	Graphite	Graphite
Linear abs coeff, cm^{-1}	63.83	6.39
Absorption correction applied	Empirical"	None
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Scan method	ω –2 $ heta$	ω –2 $ heta$
2θ range, °	4.88-124.60	4.00-45.00
Scan width,	$0.40 + 0.26 \tan \theta$	$0.43 \pm 0.35 \tan \theta$
Take-off angle,	6.00	2.95
Programs used	Enraf–Nonius MolEN	Enraf-Nonius MolEN
F (000)	2424.0	1248.0
<i>p</i> -factor used in weighting	0.040	0.040
Data collected	8998	40.54
Unique data	8559	4054
Data with $I > 3.0\sigma$ (I)	4118	2719
Number of variables	649	307
Largest shift-esd in final cycle, e Å ⁻³	0.04	0.12
R	0.041	0.032
R _w	0.048	0.041
Goodness-of-fit	1.125	1.172

"See ref. [15].

Table 2. Comparison of IR carbonyl stretching frequencies, v(CO), of $[Ru_2(\mu-R_2PYPR_2)(\mu-R'_2PYPR'_2)(\mu-CO)(CO)_4]$

R	R′	Y	v(CO)				
OPh	OPh	NEt	2021	1987	1948	1932	1720"
OMe	OMe	NEt	1999	1960	1929	1913	1703"
Ph	Ph	CH_2	1964	1918	1894	1872	1700*
Me	Me	CH_2	1953	1904	1881	1855	1686*
Ph	Me	CH_2	1951	1912	1895	1867	1682*

"Cyclohexane solution sample [5].

^b KBr pellet.

2.9073(9) Å, as compared with 2.8928(8) for 2 [7]. Similarly Ru—C and Ru—P bond distances are rather similar for 3 and 2. Generally, core bond distances are longer in 3 than in the related diphosphazane, $[Ru_2{\mu-(MeO)_2PN(Et)P(OMe)_2}_2(\mu-CO)(CO)_4]$ [5].

Substituting dcypm in the high-pressure synthesis resulted in the formation of the mononuclear ruthenium complex $[Ru(dcypm)(CO)_3]$ (5). This is likely to be the result of the steric bulk of the

cyclohexyl rings. Dinuclear dcypm-bridged complexes do, however, exist [20]. Complex 5 shows a singlet in the ³¹P NMR at δ -3.3 and three v(CO) bands in the IR at 1981, 1899 and 1880 cm⁻¹. This is characteristic of axial, equatorial coordinated ruthenium bis(phosphine) complexes [21–23]. The v(CO) bands occur lower in energy than the similar bis(diphenylphosphino)ethane (dppe) complex, [Ru(dppe)(CO)₃ $(v(CO) = 1997, 1942, 1885 \text{ cm}^{-1})$ [21] owing to the increased basicity of dcypm. The large shift of the ³¹P NMR signal of 5 higher field (-3.3 ppm) compared with the bridging diphosphine complexes 2-4 is characteristic of the four-membered RuP₂C ring of a chelating methylene diphosphine. The ring contributions, Δ_R , to the ³¹P chemical shifts of chelating methylene diphosphine complexes can be greater than - 50 ppm [24].

An ORTEP view of $[Ru(dcypm)(CO)_3]$ (5) is shown in Fig. 2. Crystal data and data collection parameters are given in Table 1. Selected bond distances and angles are given in Table 4. The complex is mononuclear and five-coordinated about ruthenium. The Ru—C bond distances are 1.884(7), 1.894(6) and



Fig. 1. An ORTEP view of $[Ru_2(\mu\text{-dppm})_2(\mu_2\text{-CO})(CO)_4]$ (3)

able 3. Selected bond distances	(Å) and angles ()) for [Ru ₂ (d	$(\mu - CO)(CO) \cdot 1 \cdot 2CH_2CN$ (3)

Ru(1)—Ru(2)	2.9073(9)	Ru(2)—C(1)	2.139(9)
Ru(1) - P(11)	2.331(2)	Ru(1) - C(21)	1.86(1)
Ru(1) - P(12)	2.339(2)	Ru(2)C(22)	1.93(1)
Ru(1) - C(1)	2.132(9)	O(1) - C(1)	1.16(1)
Ru(1) - C(11)	1.86(1)	O(11)—C(11)	1.15(1)
Ru(1)—C(12)	1.92(1)	O(12)C(12)	1.15(1)
Ru(2)—P(21)	2.340(3)	O(21)—C(21)	1.15(1)
Ru(2)—P(22)	2.349(2)	O(22)—C(22)	1.14(1)
P(11) - Ru(1) - P(12)	176.33(9)	P(21)Ru(2)C(21)	89.1(3)
P(11) - Ru(1) - C(1)	92.1(2)	Ru(1)-C(1)-Ru(2)	85.8(3)
P(11) - Ru(1) - C(11)	89.5(3)	P(21) - Ru(2) - C(22)	89.8(3)
P(11) - Ru(1) - C(12)	90.9(3)	P(22) - Ru(2) - C(1)	93.1(2)
P(12) - Ru(1) - C(1)	88.2(2)	P(22) - Ru(2) - C(21)	87.7(3)
P(12) - Ru(1) - C(11)	87.0(3)	P(22) Ru(2)—C(22)	92.4(3)
P(12) - Ru(1) - C(12)	91.3(3)	C(1) - Ru(2) - C(21)	106.1(4)
C(1) - Ru(1) - C(11)	107.6(4)	C(1) - Ru(2) - C(22)	141.8(4)
C(1) - Ru(1) - C(12)	139.9(4)	C(21)—Ru(2)—C(22)	111.9(4)
C(11) - Ru(1) - C(12)	112.3(4)	Ru(1) - C(1) - O(1)	137.3(8)
P(21)—Ru(2)—P(22)	176.58(9)	Ru(2) - C(1) - O(1)	136.9(8)
P(21) - Ru(2) - C(1)	86.8(2)		



Fig. 2. An ORTEP view of [Ru(dcypm)(CO)₃] (5)

Table 4. Selected bond distances (Å) and angles (°) for $[Ru(dcypm)(CO)_3]$ (5)

			The second	
Ru - P(1) 2.	370(1)	Ru—C(3)	1.909(7)	
Ru—P(2) 2.	378(1)	O(1)—C(1)	1.160(7)	
Ru—C(1) 1.	884(7)	O(2)C(2)	1.152(6)	
Ru—C(2) 1.	894(6)	O(3)—C(3)	1.137(7)	
P(1)— Ru — $P(2)$	70.71(4)	C(1)—Ru-	—C(2)	116.8(2)
P(1)— Ru — $C(1)$	95.3(2)	C(1)—Ru	C(3)	92.6(3)
P(1)— Ru — $C(2)$	92.8(2)	C(2)—Ru	-C(3)	93.6(3)
P(1)— Ru — $C(3)$	166.4(2)	Ru - P(1)-	-C(B)	96.5(2)
P(2)— Ru — $C(1)$	119.7(2)	Ru—P(2)-	-C(B)	96.2(2)
P(2)— Ru — $C(2)$	122.1(2)	P(1) - C(E)	B)—P(2)	96.3(2)
P(2)— Ru — $C(3)$	95.7(2)			

1.909(7) Å and the Ru—P distances are 2.370(1) and 2.378(1) Å, not significantly different from those reported for $[Ru(PMe_3)_2(CO)_3]$ and $[Ru(PPh_3)_2(CO)_3]$ [13,14]. The P—Ru—P angle is quite narrow at 70.71(4)°.

We have thus shown the generality of the highpressure synthesis of mono- and di-nuclear ruthenium complexes from $[Ru(CO)_{12}]$ and bis(dialkylphosphino)- or bis(diarylphosphino)-methanes. The novel mixed-ligand complex $[Ru_2(\mu-dmpm)(\mu-dppm))$ $(\mu-CO)(CO)_4]$ has also been prepared by this method. The selectivity of this method for preparing mononuclear vs dinuclear products appears to depend on the steric requirements of the diphosphine ligand.

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