Reactivity of Trinuclear Ruthenium Complexes involving Bis(diphenylphosphino)methane (dppm) as a Bridging Ligand: Facile Declusterification of $[Ru_3(CO)_8(\mu\text{-dppm-}PP')_2]$ in the Presence of Iodine and the Crystal Structure of $[Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-dppm-}PP')]$ †

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$[Ru_3(CO)_8(\mu\text{-dppm-}PP')_2]$ reacts with iodine in toluene to yield a mixture of $[Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-dppm-}PP')]$ and $[RuI_2(CO)_2(\text{dppm-}PP')]$. Both complexes have been characterized spectroscopically. The structure of the binuclear species $[Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-dppm-}PP')]$ has been determined using *X*-ray analysis. The two metal centres are connected by a bridging dppm ligand and two bridging iodide atoms. The metal–metal bonding distance is 2.7074(6) Å.

Recent observations of the ruthenium-catalysed conversion of synthesis gas to a mixture of methanol and ethylene glycol in the presence of halide promoters[1,2] have renewed interest in carbonyl–halide clusters.

In earlier studies of the complex $[Ru_3(CO)_8(\mu\text{-dppm})_2]$, one of our goals was to estimate the efficiency of the bridging bis(diphenylphosphino)methane (dppm) ligand in preserving the Ru_3 framework in reactions which might be expected to induce aggregation[3] or degradation[4] of the cluster. The reaction with halogens is also significant for this purpose. Typically, $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ display a different reactivity towards halogens which may reflect a difference in the stability of their metal–metal bonds.[5] Complete fragmentation of $[Ru_3(CO)_{12}]$ occurs to yield mononuclear $[Ru(CO)_4X_2]$ (X = halide) which next trimerizes as $[Ru_3(CO)_{12}X_6]$.[6] By contrast, oxidative-addition of halogens to $[Os_3(CO)_{12}]$ affords linear complexes $[Os_3(CO)_{12}X_2]$[7] which then lose CO and cyclize, providing $[Os_3(CO)_{10}X_2]$.[8] With these results in mind, we attempted the reaction of $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ with iodine to check the effect of the presence of two bridging dppm ligands on the cluster reactivity.

Experimental

General Comments.—All reactions were carried out under nitrogen using Schlenk-tube techniques. All organic solvents were reagent grade and were distilled prior to use. $[Ru_3(CO)_{12}]$[9] and $[Ru_3(CO)_8(\mu\text{-dppm})_2]$[10] were prepared according to published procedures. The latter complex was recrystallized as $[Ru_3(CO)_8(\mu\text{-dppm})_2]\cdot 2Me_2CO$.[11] Analytical data were obtained from the 'Service Central de Microanalyses du C.N.R.S.' Infrared spectra in the ν(CO) region were recorded on a Perkin-Elmer 225 spectrophotometer. These spectra were calibrated against water vapour absorptions. N.m.r. spectra were recorded on a Brucker WH 90 Fourier-transform spectrometer. Proton chemical shifts are reported as δ values in p.p.m. downfield from internal $SiMe_4$ whilst ^{31}P chemical shifts are reported as δ values in p.p.m. downfield from external H_3PO_4 (85%). Mass spectra were recorded on a Varian Mat 311 A spectrometer, using a direct inlet probe (electron impact) at 65 °C.

Preparation of the Complexes.—Crystals of $[Ru_3(CO)_8(\mu\text{-dppm})_2]\cdot 2Me_2CO$ (400 mg, 0.28 mmol) were dissolved in toluene (15 cm^3). Crystals of iodine (144 mg, 0.57 mmol) were added and the solution was heated at 75 °C for 2 h. After cooling, the solution was reduced in volume and chromatographed on a silica gel column (Kieselgel 60, Merck Art. 7734). Elution with toluene–heptane (1:1) afforded an orange band. Further elution with dichloromethane gave a yellow band. The first fraction was subsequently characterized as $[Ru_2I_2(CO)_4(\mu\text{-dppm})]$ and the second identified as $[RuI_2(CO)_2(\text{dppm})]$.

$[Ru_2I_2(CO)_4(\mu\text{-dppm})]$ (65 mg, 12%) (Found: C, 36.1; H, 2.3; I, 24.4; Ru, 19.8%; M^+, 954. $C_{29}H_{22}I_2O_4P_2Ru_2$ requires C, 36.5; H, 2.3; I, 26.6; Ru, 21.2%; M^+, 954). I.r. (cyclohexane): $\nu_{max.}$ at 2 025s, 2 005vs, 1 965s, and 1 952w cm^{-1} (CO); δ_H (90.02 MHz, $CDCl_3$ solvent, standard $SiMe_4$), 7.35 (20 H, m, 4 C_6H_5), 4.9 [2 H, m, *J*(PH) 11 Hz, CH_2]; δ_P (36.45 MHz, $CDCl_3$ solvent, external standard H_3PO_4), 17.4 (2 P, s, terminal P). $[RuI_2(CO)_2(\text{dppm})]$ (320 mg, 59%) (Found: C, 39.4; H, 2.7; I, 31.0; Ru, 10.4. $C_{27}H_{22}I_2O_2P_2Ru$ requires C, 40.8; H, 2.8; I, 31.9; Ru, 12.7%). I.r. (CH_2Cl_2): $\nu_{max.}$ at 2 065vs and 2 013s cm^{-1} (CO); δ_H (90.02 MHz, CD_2Cl_2 solvent, standard $SiMe_4$), 7.4 (20 H, m, 4 C_6H_5), 5.06 [2 H, t, *J*(PH) 10.6 Hz, CH_2]; δ_P [36.45 MHz, $(CD_3)_2CO$ solvent, external standard H_3PO_4], 23.7 (2 P, s, terminal P).

Under the same conditions as above, reaction of $[Ru_2I_2(CO)_4(\mu\text{-dppm})]$ with excess of iodine gave $[RuI_2(CO)_2(\text{dppm})]$ quantitatively.

X-Ray Structure Analysis of $[Ru_2I_2(CO)_4(\mu\text{-dppm})]$.—*Crystal data.* $C_{29}H_{22}I_2O_4P_2Ru_2$, M = 952.4, monoclinic, a = 10.659(1), b = 23.527(2), c = 12.515(1) Å, β = 90.69(1)°, U = 3 138(1) Å^3 [by least-squares refinement on diffractometer angles for 25 reflections in the range $24 < 2\theta < 26°$ using Mo-K_α radiation (λ = 0.7107 Å)], space group $P2_1/n$ (alt. $P2_1/c$, no. 14), Z = 4, D_c = 2.01 g cm^{-3}. Parallepipedic platelet. Crystal dimensions (distances to faces from centre): 0.239 (100, $\bar{1}00$) × 0.037 (010, $0\bar{1}0$) × 0.016 (001, $00\bar{1}$) mm, μ(Mo-K_α) = 30.6 cm^{-1}.

Data collection and processing. For full details of experimental techniques used see ref. 3. Enraf-Nonius CAD4

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† μ-Bis(diphenylphosphino)methane-*PP'*-di-μ-iodo-bis(dicarbonylruthenium) (*Ru–Ru*).

Supplementary data available (No. SUP 56463, 3 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Atomic co-ordinates of independent non-hydrogen atoms for $[Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-dppm-}PP')]$ with estimated standard deviations (e.s.d.s) in parentheses

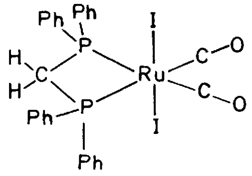
Atom	*x*	*y*	*z*
I(1)	0.868 42(3)	0.312 71(2)	0.242 61(3)
I(2)	0.898 97(4)	0.433 75(2)	0.063 69(3)
Ru(1)	0.725 42(4)	0.347 94(2)	0.068 89(3)
Ru(2)	0.753 10(4)	0.416 84(2)	0.240 84(3)
P(1)	0.560 7(1)	0.294 49(6)	0.129 7(1)
P(2)	0.575 6(1)	0.378 78(6)	0.315 29(10)
C(1)	0.765 1(6)	0.299 6(3)	−0.049 3(5)
O(1)	0.782 0(6)	0.272 6(3)	−0.122 9(4)
C(2)	0.617 7(5)	0.398 9(3)	−0.000 8(4)
O(2)	0.557 9(4)	0.430 6(2)	−0.042 4(3)
C(3)	0.837 5(5)	0.442 6(3)	0.367 7(5)
O(3)	0.885 4(5)	0.456 7(2)	0.444 2(4)
C(4)	0.679 1(5)	0.487 3(3)	0.217 2(5)
O(4)	0.640 2(4)	0.532 1(2)	0.204 5(4)
C(5)	0.541 9(4)	0.305 4(2)	0.273 7(4)

diffractometer, $\omega/2\theta$ scan mode with ω scan width $0.8 + 0.35 \tan\theta$, ω scan speed $2^\circ\ min^{-1}$, graphite-monochromated Mo-K_α radiation; 5 994 reflections measured ($1 < \theta < 25^\circ$), giving 4 393 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. Intensities corrected for absorption,[3] minimum and maximum transmission factors = 0.405, 0.792. No intensity decay.

Structure analysis and refinement. Direct methods (location of I and Ru atoms). The model was extended through a combination of Fourier difference maps and full-matrix least-squares refinements. Phenyl rings were treated as rigid groups (idealized D_{6h} symmetry, C–C 1.395, C–H 0.95 Å). Anisotropic thermal parameters were used for all other non-hydrogen atoms. Final R' and R values were 0.035 and 0.031 respectively. Programs and computer used and sources of scattering factor data are given in ref. 3. Atomic co-ordinates are given in Table 1.

Results and Discussion

Electrophilic attack of I_2 at the carbonyl cluster $[Ru_3(CO)_8(\mu\text{-dppm})_2]$ proceeds with cluster fragmentation to yield a mixture of $[Ru_2I_2(CO)_4(\mu\text{-dppm})]$ and $[RuI_2(CO)_2(dppm)]$. This result is comparable with that obtained in the case of $[Ru_3(CO)_9L_3]$ [L = PPh_3, PBu^n_3 or $P(OPh)_3$] which was shown to yield $[Ru_2X_2(CO)_6L_2]$ and $[RuX_2(CO)_3L]$ upon reaction with halogens.[12] Noticeably, the use of bridging dppm ligands *vs.* terminal phosphines does not modify the course of the fragmentation reaction. However, the nature of the mononuclear complex is different, since both P atoms are co-ordinated to the Ru centre in the case of dppm. Related examples of mononuclear complexes $[RuCl_2(CO)_2L_2]$ (L = phosphine) have been reported.[13–15] Spectroscopic data for $[RuI_2(CO)_2(dppm)]$ are consistent with the structure depicted below, in agreement with related observations regarding $[RuCl_2(CO)_2(dppm)]$.[13]



The binuclear complex $[Ru_2I_2(CO)_4(\mu\text{-dppm})]$ may be compared with related halogen-bridged species $[Ru_2Cl_2(CO)_4\{PBu^t_2(C_6H_4Me\text{-}p)\}_2]$[16] and $[Ru_2I_2(CO)_4(PPh_3)_2]$[17] which are available through different routes.

Table 2. Selected interatomic distances (Å) with e.s.d.s in parentheses for $[Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-dppm-}PP')]$

Ru(1)–Ru(2)	2.7074(6)	Ru(1)–I(1)	2.7672(6)
		Ru(1)–I(2)	2.7395(5)
Ru(1)–P(1)	2.297(1)	Ru(2)–I(1)	2.7410(5)
Ru(2)–P(2)	2.300(1)	Ru(2)–I(2)	2.7521(6)
Ru(1)–C(1)	1.918(7)	C(1)–O(1)	1.135(7)
Ru(1)–C(2)	1.869(6)	C(2)–O(2)	1.107(6)
Ru(2)–C(3)	1.913(6)	C(3)–O(3)	1.131(7)
Ru(2)–C(4)	1.859(6)	C(4)–O(4)	1.142(7)
P(1)–C(5)	1.835(5)		
P(2)–C(5)	1.837(5)		

Table 3. Selected bond angles (°) with e.s.d.s in parentheses for $[Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-dppm-}PP')]$

Ru(1)–I(1)–Ru(2)	58.88(2)	Ru(1)–Ru(2)–I(1)	61.04(2)
Ru(1)–I(2)–Ru(2)	59.08(2)	Ru(1)–Ru(2)–I(2)	60.23(2)
		Ru(2)–Ru(1)–I(1)	60.08(2)
Ru(1)–Ru(2)–P(2)	90.38(4)	Ru(2)–Ru(1)–I(2)	60.69(2)
Ru(2)–Ru(1)–P(1)	98.11(4)		
		I(1)–Ru(1)–I(2)	82.75(2)
Ru(1)–Ru(2)–C(3)	153.4(2)	I(1)–Ru(2)–I(2)	83.00(2)
Ru(1)–Ru(2)–C(4)	111.5(2)		
Ru(2)–Ru(1)–C(1)	161.0(2)	I(1)–Ru(1)–P(1)	89.53(4)
Ru(2)–Ru(1)–C(2)	92.2(2)	I(2)–Ru(1)–P(1)	158.51(3)
		I(1)–Ru(2)–P(2)	91.13(4)
I(1)–Ru(1)–C(1)	107.7(2)	I(2)–Ru(2)–P(2)	149.09(3)
I(1)–Ru(1)–C(2)	152.7(2)		
I(2)–Ru(1)–C(1)	105.3(2)	Ru(1)–P(1)–C(5)	110.0(2)
I(2)–Ru(1)–C(2)	85.8(2)	Ru(2)–P(2)–C(5)	114.2(2)
I(1)–Ru(2)–C(3)	94.0(2)		
I(1)–Ru(2)–C(4)	171.2(2)	P(1)–Ru(1)–C(1)	96.1(2)
I(2)–Ru(2)–C(3)	111.0(2)	P(1)–Ru(1)–C(2)	92.2(2)
I(2)–Ru(2)–C(4)	89.2(2)	P(2)–Ru(2)–C(3)	99.7(2)
		P(2)–Ru(2)–C(4)	93.6(2)
C(1)–Ru(1)–C(2)	99.2(3)		
C(3)–Ru(2)–C(4)	92.5(3)	P(1)–C(5)–P(2)	112.7(2)

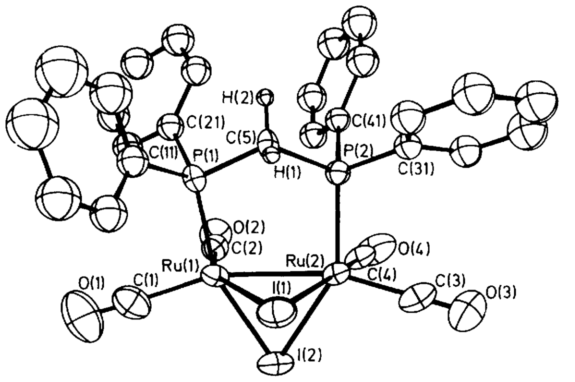


Figure. ORTEP diagram of $[Ru_2(\mu\text{-}I)_2(CO)_4(\mu\text{-dppm-}PP')]$. Thermal ellipsoids are shown at the 50% probability level

Molecular Structure of $[Ru_2I_2(CO)_4(\mu\text{-dppm})]$.—A perspective view of the complex is shown in the Figure. Selected interatomic distances and bond angles are given in Tables 2 and 3, respectively. The structure consists of two Ru centres which are bridged by the bis(diphenylphosphino)methane ligand and two iodine atoms. The octahedral environment of each metal atom is achieved with 2 CO ligands. The metal–metal separation, 2.7074(6) Å, is consistent with the presence of a metal–metal bond which is also inferred from electron-counting schemes (34e species). The bridging iodine atoms I(1) and I(2) are respectively *cis* and *trans* relative to both P atoms. Carbonyl groups C(1)–O(1) and C(3)–O(3) are *trans* to the metal–metal vector, while C(2)–O(2) and C(4)–O(4) are *trans* to I(1). A *trans* shortening effect of the iodide atom I(1) on the distances Ru(1)–C(2) and Ru(2)–C(4) is observed.[18]

References

1 J. F. Knifton, *J. Am. Chem. Soc.*, 1981, **103**, 3959.
2 B. D. Dombek, *J. Am. Chem. Soc.*, 1981, **103**, 6508.
3 G. Lavigne, N. Lugan, and J. J. Bonnet, *Organometallics*, 1982, **1**, 1040 and refs. therein.
4 G. Lavigne, N. Lugan, and J. J. Bonnet, *Nouv. J. Chim.*, 1981, **5**, 423.
5 A. J. Deeming, in 'Transition Metal Clusters,' ed. B. F. G. Johnson, John Wiley and Sons, New York, 1980, p. 391.
6 B. F. G. Johnson, J. Lewis, and I. G. Williams, *Chem. Commun.*, 1968, 861.
7 N. Cook, L. Smart, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1977, 1744.
8 A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1969, **17**, 40.
9 A. Mantovani and S. Cenini, *Inorg. Synth.*, 1976, **16**, 47.
10 G. Lavigne and J. J. Bonnet, *Inorg. Chem.*, 1981, **20**, 2713.
11 G. Lavigne, N. Lugan, and J. J. Bonnet, *Acta Crystallogr., Sect. B*, 1982, **38**, 1911.
12 G. Kramer, A. Pöe, and S. Amer, *Inorg. Chem.*, 1981, **20**, 1362.
13 J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, 1972, **11**, 2714.
14 D. F. Gill, B. E. Mann, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 311 and refs. therein.
15 L. M. Wilkes, J. H. Nelson, L. B. McCusker, K. Seff, and F. Mathey, *Inorg. Chem.*, 1983, **22**, 2476 and refs. therein.
16 R. Mason, K. M. Thomas, D. F. Gill, and B. L. Shaw, *J. Organomet. Chem.*, 1972, **40**, C67.
17 D. F. Jones, P. H. Dixneuf, A. Benoit, and J. Y. Le Marouille, *Inorg. Chem.*, 1983, **22**, 29.
18 A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 170.

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