

# Ruthenium carbonyl clusters containing $\text{PMe}_2(\text{nap})$ and derived ligands ( $\text{nap} = 1\text{-naphthyl}$ ): generation of naphthalene derivatives

Michael I. Bruce<sup>a,\*</sup>, Paul A. Humphrey<sup>a</sup>, Reinhard Schmutzler<sup>b</sup>,  
Brian W. Skelton<sup>c</sup>, Allan H. White<sup>c</sup>

<sup>a</sup> Department of Chemistry, University of Adelaide, Adelaide, SA 5005, Australia

<sup>b</sup> Institut für Anorganische und Analytische Chemie der Technischen Universität Carolo-Wilhelmina, 38023 Braunschweig, Germany

<sup>c</sup> Department of Chemistry, University of Western Australia, Crawley, WA 6009, Australia

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Dedicated to Professor Michael Veith on the occasion of his 60th birthday

## Abstract

Bis(dimethylphosphino)naphthalene, 1,8- $(\text{PMe}_2)_2\text{C}_{10}\text{H}_6$  (dmpn), reacts readily with  $\text{Ru}_3(\text{CO})_{12}$  or  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$  with replacement of one of the  $\text{PMe}_2$  groups by H to give  $\text{Ru}_3(\text{CO})_{12-n}\{\text{PMe}_2(\text{nap})\}_n$  ( $n = 1$  **2**, 2 **3**) or  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\{\text{PMe}_2(\text{nap})\}$  **4**; the complex  $\text{Ru}_3(\text{CO})_{10}(\text{dmpn})$  **1** is obtained only in small amount. Thermolysis of **2** or **4** gives  $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-PMe}_2(\text{C}_{10}\text{H}_5)\}(\mu\text{-dppm})_n(\text{CO})_{8-2n}$  ( $n = 0$  **5**, 1 **6**, respectively) containing  $\mu_3$ -naphthalene groups.  
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## 1. Introduction

The formation and subsequent chemistry of metal carbonyl clusters containing Group 15 ligands continues to excite interest, both from a synthetic point of view and because of their possible involvement in catalytic processes [1]. We have recently described the complexes formed in reactions between triruthenium and triosmium cluster carbonyls and 1,8-bis(diphenylphosphino)naphthalene, 1,8- $(\text{PPh}_2)_2\text{C}_{10}\text{H}_6$  (dppn), from which products formed by C–H and C–P bond cleavage in both the Ph and  $\text{C}_{10}$  rings were isolated [2,3]. A cluster containing an unaltered dppn ligand was not detected with  $\text{Ru}_3(\text{CO})_{12}$ . In a move to restrict subsequent reactions to the  $\text{C}_{10}$  ring, we have also studied similar chemistry of the methyl analogue of dppn, 1,8- $(\text{PMe}_2)_2\text{C}_{10}\text{H}_6$

(dmpn) with ruthenium clusters. These results are presented in this paper.

## 2. Results and discussion

The reaction between  $\text{Ru}_3(\text{CO})_{12}$  and dmpn was carried out in thf at r.t. Addition of trimethylamine oxide ( $\text{ONMe}_3$ , tmno) to activate the carbonyl resulted in a rapid colour change to deep red, after which t.l.c. showed the presence of four components. Separation by preparative t.l.c. on silica gel afforded recovered  $\text{Ru}_3(\text{CO})_{12}$  (15%), together with three phosphine-substituted cluster complexes identified as  $\text{Ru}_3(\text{CO})_{10}(\text{dmpn})$  (**1**) and  $\text{Ru}_3(\text{CO})_{12-n}\{\text{PMe}_2(\text{nap})\}_n$  [ $n = 1$  (**2**), 2 (**3**)] by elemental analyses, spectroscopic methods and for **1** and **3**, single-crystal X-ray structure determinations.

Complex **1**, which was isolated in only 6% yield, gave an IR  $\nu(\text{CO})$  spectrum containing only terminal CO bands, while the  $^1\text{H}$  NMR spectrum contained a characteristic virtual triplet at  $\delta$  1.88 for the A part of an

\* Corresponding author. Fax: +618 8303 4358.

E-mail address: [michael.bruce@adelaide.edu.au](mailto:michael.bruce@adelaide.edu.au) (M.I. Bruce).

$A_6XX'A'_6$  spin system resulting from the two  $\text{PMe}_2$  groups; multiplets between  $\delta$  7.59 and 8.01 were assigned to the  $\text{C}_{10}\text{H}_6$  portion of the dmpn ligand. The electrospray mass spectrum (ES-MS) was obtained from a methanol solution containing NaOMe as an ionisation aid and contained ions at  $m/z$  856 and 828, assigned to  $[\text{M} + \text{Na} - n\text{CO}]^+$  ( $n = 0, 1$ ).

The major product was **2**, which was shown to be a complex containing  $\text{PMe}_2(\text{nap})$  as the Group 15 ligand. Isolated in 16% yield, this orange-red derivative has an IR  $\nu(\text{CO})$  pattern in the terminal region similar to those of many other  $\text{Ru}_3(\text{CO})_{11}(\text{L})$  complexes [4]. In this case, the Me resonance in the  $^1\text{H}$  NMR spectrum was a simple doublet at  $\delta$  2.13 showing a 8.4 Hz coupling to  $^{31}\text{P}$ . In the negative ion ES-MS (solution in MeOH/NaOMe), ions at  $m/z$  832, 804 and 776 were assigned to  $[\text{M} + \text{OMe} - n\text{CO}]^-$  ( $n = 0-2$ ). A single-crystal X-ray structure determination showed that **3** was  $\text{Ru}_3(\text{CO})_{10}\{\text{PMe}_2(\text{nap})\}_2$ , which had a terminal  $\nu(\text{CO})$  spectrum and a doublet similar to that of **2** at  $\delta$  2.04 [ $J(\text{HP})$  8.4 Hz]. The ES-MS spectrum, obtained from solutions containing NaOMe, contained both  $[\text{M} + \text{Na}]^+$  and  $[\text{M} + \text{OMe}]^-$ , at  $m/z$  984 and 992, respectively.

We were not able to avoid the ready loss of the  $\text{PMe}_2$  fragment from dmpn in these reactions, which seems to occur more rapidly than substitution of CO in  $\text{Ru}_3(\text{CO})_{12}$ . The fate of this  $\text{PMe}_2$  group remains unknown, although intractable materials in the t.l.c. plate may have resulted from further reactions of a complex such as  $\{\text{Ru}(\mu\text{-PMe}_2)(\text{CO})_3\}_2$ .

Only one complex was isolated from the reaction between dmpn and  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$ , carried out under similar conditions to the reaction with the parent carbonyl. Dark red crystals of  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\{\text{PMe}_2(\text{nap})\}$  (**4**) were obtained in 45% yield. The IR spectrum contained a relatively simple  $\nu(\text{CO})$  pattern, while the  $^1\text{H}$  NMR spectrum contained a doublet at  $\delta$  2.04 [ $J(\text{HP})$  8.4 Hz], together with the  $\text{CH}_2$  resonance at  $\delta$  4.21 and phenyl proton multiplets between  $\delta$  7.34 and 8.45. The ES-MS contained several ions formed by loss of CO or  $\text{PMe}_2(\text{nap})$  ligands in addition to  $\text{M}^+$  at  $m/z$  1129. The molecular structure was confirmed by an X-ray determination.

The high reactivity of the dmpn ligand suggested that thermolysis of complexes **2** and **4** might result in further degradation of the Group 15 ligand. Accordingly, heating a solution of **2** in thf overnight and separation of the products by preparative t.l.c. gave a major orange fraction which contained the hydrido cluster  $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-PMe}_2(\text{C}_{10}\text{H}_5)\}(\text{CO})_8$  (**5**), isolated in 64% yield. The spectroscopic properties were consistent with the molecular structure, determined from an X-ray study. In addition to a terminal  $\nu(\text{CO})$  spectrum, the  $^1\text{H}$  NMR spectrum contained resonances at  $\delta$  -19.09 and -16.02 assigned to cluster-bonded H atoms, which showed double doublets with  $J(\text{HP})$  32.1 and 9.9 Hz, respectively,

and  $J(\text{HH})$  1.2 Hz. In the light of the crystal structure, these can be assigned to H atoms bridging the Ru(1)–Ru(2, 3) vectors, which are the longest Ru–Ru separations. The Me resonances are a doublets at  $\delta$  1.96 and 2.01, and the  $\text{C}_{10}\text{H}_5$  give five multiplets between  $\delta$  7.43 and 8.07. The negative ion ES-MS spectrum contains  $\text{M}^-$  and  $[\text{M} + \text{OMe}]^-$  at  $m/z$  717 and 748, respectively.

Similar treatment of **4** afforded the dppm analogue of **5** as orange crystals in 86% yield, as confirmed by an X-ray structure determination. The  $^1\text{H}$  NMR spectrum of the product,  $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-PMe}_2(\text{C}_{10}\text{H}_5)\}(\mu\text{-dppm})(\text{CO})_6$  (**6**) shows the presence of two isomers in solution in 85/15 ratio. The major isomer gives Ru–H signals at  $\delta$  -17.94 and -15.53, while the minor component gives Ru–H resonances at  $\delta$  -19.08 and -15.06, all with multiplet structure. Four P–Me doublets are found at  $\delta$  1.60, 1.91 (major) and 1.71, 1.97 (minor). These data are consistent with differentiation of the two P–Me groups in each isomer as a result of the presence of the dppm ligand and the two isomers can be formulated at **6a** and **6b**. The ES-MS spectra obtained in the presence of NaOMe, contain  $[\text{M} + \text{Na}]^+$  and  $[\text{M} - \text{H}]^-$  at  $m/z$  1068 and 1044, respectively.

## 2.1. Molecular structures

The X-ray structures of **1** and **3–6** were determined, projections of single molecules of each being given in Figs. 1–5 and selected bond parameters being listed in Table 1. All molecules are based on a closed  $\text{Ru}_3$  cluster to which the Group 15 ligands and only terminal CO groups are attached and all have 48-electron counts.

In **1**, chelation of the dmpn ligand is similar to that found in the dppm analogue **4**, with Ru–P distances of 2.2920, 2.2966(7) Å<sup>2</sup>, somewhat shorter than the Ru–P separations found in **3** [2.3461, 2.3438(7) Å] and **4** [2.349(3)  $\text{PMe}_2(\text{nap})$ ; 2.329, 2.330(3) Å (dppm)]. These Ru–P separations are similar to those found in many complexes containing monodentate  $\text{PR}_3$  ligands and / or dppm ligands listed in the Cambridge Data Base [5]. The P(1)···P(2) separation in **1** is 3.1409(9) Å (see Table 2).

With one exception, the CO groups are terminally bonded to their Ru atoms, with the expected differences in Ru–C distances for axial [1.920–1.969(3) for **1**, 1.927–1.940(3) for **3**, 1.92–1.95(1) Å for **4**] and equatorial [1.902–1.913(3) for **1**, 1.872–1.923(3) for **3**, 1.89–1.92(1) Å for **4**] groups (with respect to the  $\text{Ru}_3$  plane) [cf.  $\text{Ru}_3(\text{CO})_{12}$ , where average values are Ru–CO(ax) 1.942(5), Ru–CO(eq) 1.921(5) Å] [7]. The exception is CO(31) in **1**, which is bent towards Ru(1) [R(1,3)–C(31) 1.900, 2.501(3) Å; Ru(1,3)–C(31)–O(31) 123.6°, 152.4(2)°]. This bending is the result of a twist about the Ru–Ru vectors, which in the parent carbonyl would result in a change from  $D_{3d}$  to  $D_3$  symmetry, and brings CO(31) closer to a bridging position. However, there is

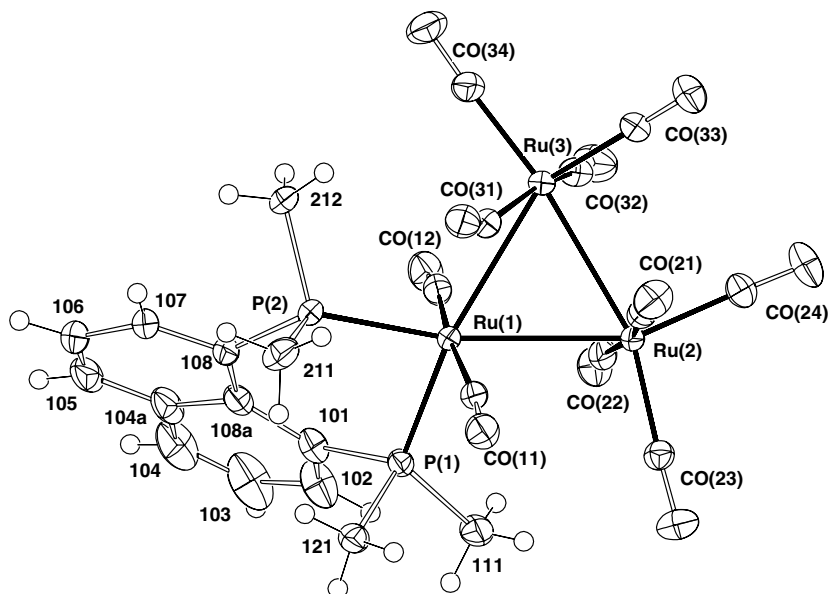


Fig. 1. Projection of a molecule of  $\text{Ru}_3(\text{CO})_{10}(\text{dmpn})$  (**1**), perpendicular to the  $\text{Ru}_3$  plane.

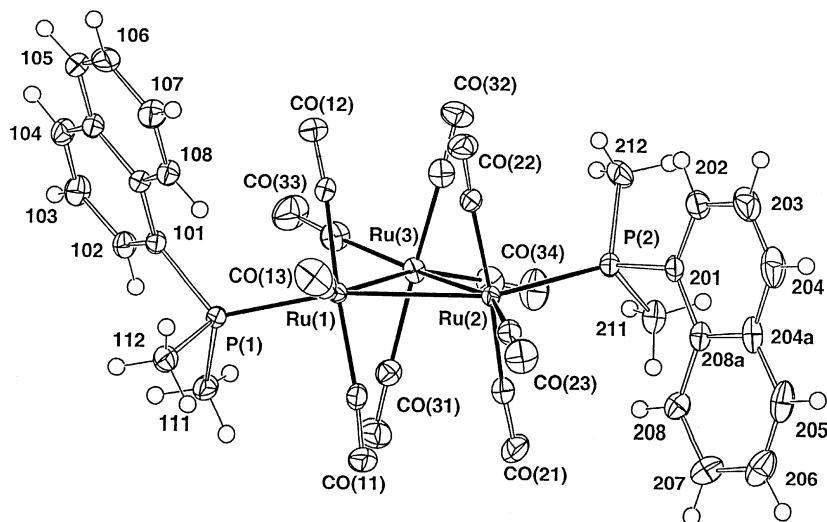


Fig. 2. Projection of a molecule of  $\text{Ru}_3(\text{CO})_{10}\{\text{PMe}_2(\text{nap})\}_2$  (**3**), perpendicular to the  $\text{Ru}_3$  plane.

no  $\nu(\text{CO})$  absorption in the  $\mu\text{-CO}$  region, the lowest frequency band being at  $1930\text{ cm}^{-1}$ . This feature of the structure of complexes  $\text{Ru}_3(\text{CO})_{12-n}(\text{PR}_3)_n$  has been noted on previous occasions [6]. The torsion angles  $\text{OC}(n1)\text{-Ru}(n)\text{-Ru}(n+1)\text{-CO}((n+1)0)$  are  $-40.1^\circ$ ,  $-43.2^\circ$  and  $-40.2(1)^\circ$  [in **1**, containing the chelating dmpn ligand on  $\text{Ru}(1)$ ], but considerably less for the di- and tri-substituted complexes [ $27.7^\circ$ ,  $28.2^\circ$ ,  $25.3(1)^\circ$  for **3**,  $23.8^\circ$ ,  $23.5^\circ$ ,  $25.9(4)^\circ$  for **4**].

The  $\text{Ru}\text{-Ru}$  separations in **1**, **3** and **4** range between 2.8365(4) and 2.8918(3) (for **1**), 2.8430 and 2.8810(3) (for **3**) and 2.864 and 2.873(1) Å (for **4**), values which are similar to those found for other analogous complexes and which may also be compared with the aver-

age  $\text{Ru}\text{-Ru}$  separations in  $\text{Ru}_3(\text{CO})_{12}$  [2.8515, 2.8595(4) Å] [7] and  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$  [2.834–2.860(1) Å; the shortest bond is bridged by dppm] [8]. The differences result from steric interactions of the Group 15 ligand substituents with the CO groups, which result in the previously reported *cis* elongation of the  $\text{Ru}\text{-Ru}$  vector. An interesting crystal packing is found in **3**, inversion-related naphthyl groups at either end of each molecule packing in sheets about  $x = 0, 0.5$ .

The molecular structures of **5** and **6** are closely related, two CO groups on adjacent Ru atoms in the former being replaced by the bridging dppm ligand in **6**. The  $\text{Ru}_3$  cluster supports two bridging H atoms and the Group 15 ligand, which is best described as a

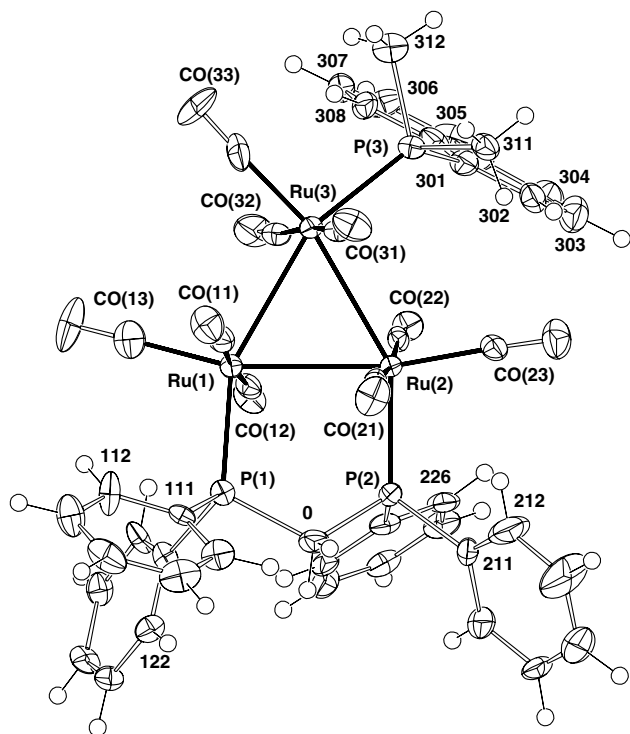


Fig. 3. Projection of a molecule of  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_9\{\text{PMe}_3(\text{nap})\}$  (**4**), perpendicular to the  $\text{Ru}_3$  plane.

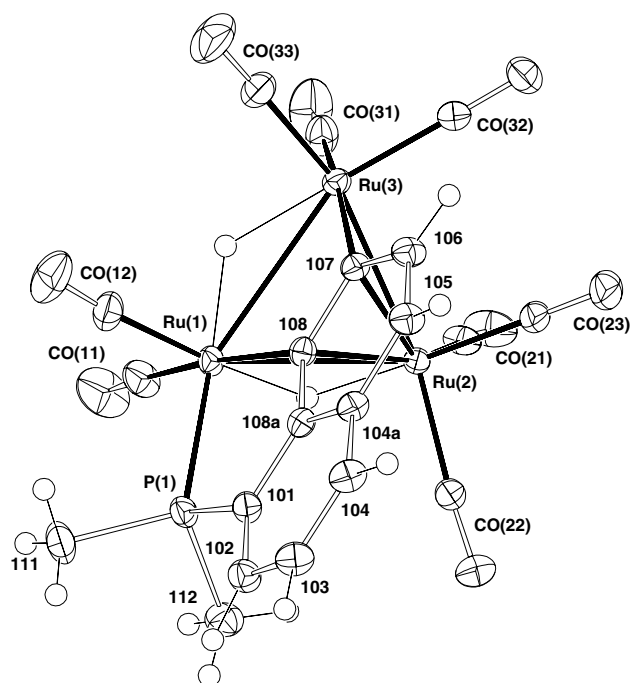


Fig. 4. Projection of a molecule of  $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-PMe}_2(\text{C}_{10}\text{H}_5)\}(\text{CO})_8$  (**5**), perpendicular to the  $\text{Ru}_3$  plane.

dimethylphosphino-naphthalene attached by the P atom and a conventional  $\mu_3$ -alkyne interaction from C(107)–C(108). The Ru–P distances [2.3211(4) in **5**, 2.301(3) Å

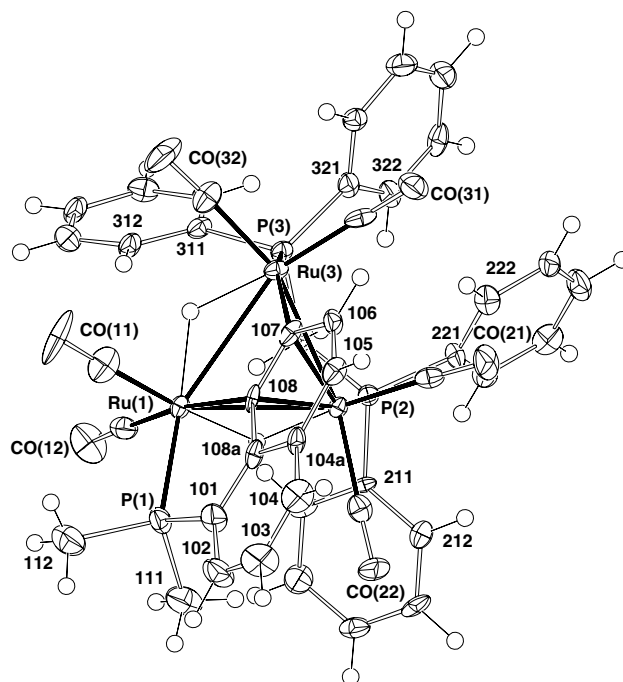


Fig. 5. Projection of a molecule of  $\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-PMe}_2(\text{C}_{10}\text{H}_5)\}(\mu\text{-dppm})(\text{CO})_6$  (**6**), perpendicular to the  $\text{Ru}_3$  plane.

in **6**] are unexceptional and are similar to those found for the dppm ligand in **6** [2.298, 2.358(3) Å]. The C<sub>10</sub> group is attached to the P atom by a single bond [1.82(1)] and to the cluster by atoms C(107, 108), which form two Ru–C  $\sigma$  bonds with Ru(1,3) [Ru(1)–C(108) 2.073(1), 2.088(9); Ru(3)–C(107) 2.093(1), 2.08(1) Å; values for **5**, **6**, respectively] and a  $\pi$  bond to Ru(2) [Ru(2)–C(107, 108) 2.359(1), 2.276(1) for **5**, 2.340(8), 2.242(7) Å for **6**]. The C(107)–C(108) bonds are 1.395(2), 1.38(1) Å, respectively. These values may be compared with those found for  $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$  [2.048, 2.122(7) and 2.213, 2.246(7) Å] [9], from which it is evident that conventional  $\mu_3$ -alkyne–Ru<sub>3</sub> interactions are present in **5** and **6**, the C<sub>10</sub>H<sub>6</sub> group being a rare example of naphthalene stabilised by attachment to an Ru<sub>3</sub> cluster. Analogous complexes containing benzyne have been known for decades [10] and, indeed, Cullen and coworkers have previously described complexes containing naphthalene isolated from reactions of  $\text{M}_3(\text{CO})_{12}$  (M = Ru, Os) and  $\text{E}(\text{nap})_3$  (E = P, As), including a direct analogue of **5**, obtained in 50% yield by heating  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{P}(\text{nap})_3$  in refluxing cyclohexane for 24 h [11].

The locations of the two  $\mu\text{-H}$  ligands can be deduced from the structural and spectroscopic results. Conventionally, the presence of a  $\mu\text{-H}$  atom is revealed by a lengthening of the M–M vector. In the present cases, both Ru(1)–Ru(3) vectors [3.0459(2), 3.049(1) Å] are considerably longer than the other two [range 2.7319(2)–2.877(1) Å], suggesting that both H atoms are bridging this vector. However, in **5**, two Ru–H

Table 1  
Selected bond distances (Å) and angles (°)

Compound	1	3	4	5	6
Bond distances					
Ru(1)–Ru(2)	2.8918(3)	2.8430(3)	2.864(1)	2.8656(2)	2.877(1)
Ru(1)–Ru(3)	2.8524(3)	2.8697(3)	2.871(1)	3.0459(2)	3.049(1)
Ru(2)–Ru(3)	2.8365(4)	2.8810(3)	2.873(1)	2.7319(2)	2.739(1)
Ru(1)–P(1)	2.2920(6)	2.3461(7)	2.329(3)	2.3211(4)	2.301(3)
Ru(1)–P(2)	2.2966(7)				
Ru(2)–P(2)		2.3438(7)	2.330(3)		2.298(3)
Ru(3)–P(3)			2.349(3)		2.358(3)
Ru(1)–C(108)				2.073(1)	2.088(9)
Ru(2)–C(107)				2.359(1)	2.340(7)
Ru(2)–C(108)				2.276(1)	2.242(8)
Ru(3)–C(107)				2.093(1)	2.08(1)
Ru(1)–CO(ax)	1.920, 1.939(3)	1.936, 1.928(3)	1.95, 1.94(1)	1.940(2)	1.925(10)
Ru(1)–CO(eq)		1.878(3)	1.92(1)	1.882(2)	1.864(9)
Ru(2)–CO(ax)	1.954, 1.935(3)	1.927, 1.934(3)	1.92, 1.94(1)	1.887(2)	
Ru(2)–CO(eq)	1.908, 1.913(3)	1.888(3)	1.89(1)	1.939, 1.893(1)	1.875, 1.901(10)
Ru(3)–CO(ax)	1.940, 1.969(3)	1.940, 1.933(3)	1.94, 1.92(1)	1.968(2)	
Ru(3)–CO(eq)	1.902, 1.911(3)	1.923, 1.911(3)	1.90(1)	1.897, 1.908(2)	1.850, 1.882(9)
P(1)–C(101)	1.832(3)	1.824(3)	1.86(1)	1.825(1)	1.819(11)
P(2)–C(201)	1.846(2) [C(108)]	1.837(3)	1.84(1)		
P(1)–C(111, 121)	1.820, 1.820(3)	1.825, 1.823(3)	1.84, 1.84(1)		1.79, 1.80(1)
P(2)–C(211, 212)	1.817, 1.830(3)	1.832, 1.820(3)	1.83, 1.83(1)		1.84, 1.82(1)

For **4**: For C(n01) read C(0) and for C(n12) read C(n21); P(3)–C(301, 311, 312) are 1.85, 1.83, 1.82(1) Å, P(1)–C(0)–P(2) 116.1(5)°.

For **5**: C(107)–C(108) 1.395(2), Ru(1)–H(1,2) 1.64, 1.65(3); Ru(2)–H(1) 1.79(2); Ru(3)–H(2) 1.83(3) Å.

For **6**: For C(212) read C(221); Ru(2)–C(107, 108) 2.340, 2.242(7); C(107)–C(108) 1.376(11); P(3)–C(311, 321) 1.849, 1.824(9), C(0)–P(2,3) 1.837, 1.847(9) Å; P(2)–C(0)–P(3) 112.0(5)°.

Table 2  
Crystal data and refinement details

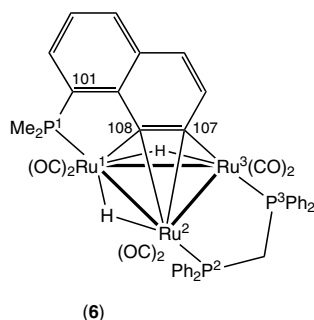
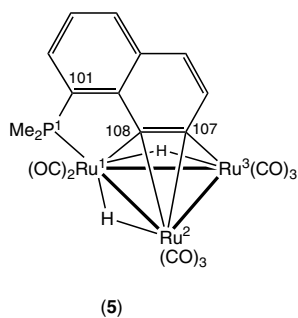
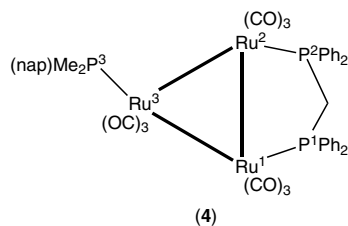
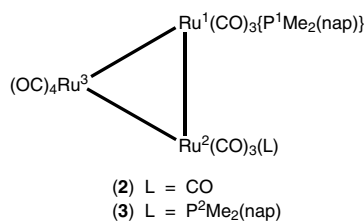
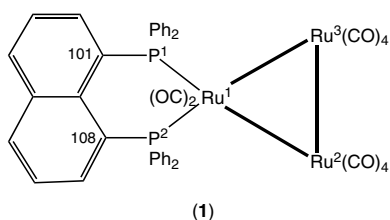
Compound	1	3	4	5	6
Formula	C <sub>24</sub> H <sub>18</sub> O <sub>10</sub> P <sub>2</sub> Ru <sub>3</sub>	C <sub>34</sub> H <sub>26</sub> O <sub>10</sub> P <sub>2</sub> Ru <sub>3</sub>	C <sub>46</sub> H <sub>35</sub> O <sub>9</sub> P <sub>3</sub> Ru <sub>3</sub>	C <sub>20</sub> H <sub>13</sub> O <sub>8</sub> P <sub>2</sub> Ru <sub>3</sub>	C <sub>43</sub> H <sub>35</sub> O <sub>6</sub> P <sub>3</sub> Ru <sub>3</sub>
Molecular weight	831.56	959.75	1127.93	715.50	1043.90
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Unit cell dimensions					
<i>a</i> (Å)	11.047(1)	26.336(1)	17.114(4)	14.9034(8)	16.702(3)
<i>b</i> (Å)	19.343(2)	8.3240(5)	12.277(3)	10.6819(6)	12.181(2)
<i>c</i> (Å)	13.130(1)	15.9908(9)	21.649(5)	14.4156(8)	20.907(4)
$\beta$ (°)	101.064(3)	99.262(1)	104.336(5)	96.079(1)	110.459(3)
<i>V</i> (Å <sup>3</sup> )	2753	3459	4407	2282	3985
<i>Z</i>	4	4	4	4	4
<i>D<sub>c</sub></i> (g cm <sup>−3</sup> )	2.00 <sub>6</sub>	1.84 <sub>2</sub>	1.17 <sub>9</sub>	2.08 <sub>2</sub>	1.73 <sub>6</sub>
$\mu$ (cm <sup>−1</sup> )	1.79	1.44	1.18	2.07	1.29
Crystal size (mm)	0.28 × 0.08 × 0.06	0.18 × 0.16 × 0.03	0.08 × 0.08 × 0.04	0.21 × 0.18 × 0.10	0.15 × 0.08 × 0.06
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.80	0.81	0.90	0.84	0.85
2 $\theta$ <sub>max</sub> (°)	75	75	50	75	53
<i>N</i> <sub>tot</sub>	56679	69290	39524	44914	36717
<i>N</i> ( <i>R</i> <sub>int</sub> )	14394 (0.037)	18117 (0.060)	7644 (0.090)	11963 (0.021)	8108 (0.085)
<i>N</i> <sub>o</sub>	10932	12520	5539	16623	5372
<i>R</i>	0.038	0.045	0.063	0.022	0.061
<i>R<sub>w</sub></i> ( <i>n<sub>w</sub></i> )	0.044 (3)	0.051 (7)	0.083 (30)	0.035 (6)	0.073 (20)

resonances are found, showing significantly different coupling to the P nucleus. For **6**, two isomeric forms are indicated, but in each, there are two Ru–H reso-

nances with different *J*(HP). These data taken together suggest that one H bridges Ru(1)–Ru(3) while the second bridges Ru(1)–Ru(2). In the analogous molecule

$\text{Ru}_3(\mu\text{-H})_2\{\mu_3\text{-PPh}_2(\text{C}_{10}\text{H}_5)\}(\text{CO})_9$ , the H atoms are shown to bridge the two longest Ru–Ru vectors; the longest separation links the two Ru atoms which are  $\sigma$ -bonded to the  $\text{C}_{10}$  system.

In conclusion, we have shown a remarkably high reactivity for the bis(phosphine) dmpn which is manifested by extremely facile cleavage of one P– $\text{C}_{10}$  bond with loss of the  $\text{PMe}_2$  group. Equally facile addition of H to this position is found with formation of the  $\text{PMe}_2(\text{nap})$  ligand found in **3** and **4**. Alternatively, further loss of H (from the 2-nap C–H bond) occurs to give **5** or **6**, which are rare examples of complexes containing a naphthalene group. These results contrast with those found in similar reactions of dppn, which are characterised by facile C–H or C–P bond cleavages giving altered ligands, such as  $\text{PPh}_2(\text{C}_{10}\text{H}_6)\text{PPh}(\text{C}_6\text{H}_4)$ ,  $\text{PPh}(\text{C}_{10}\text{H}_6)\text{-PPh}_2$  or  $\text{P}(\text{C}_{10}\text{H}_6)\text{PPh}_2$  ( $\text{C}_{10}\text{H}_6 = 1,8\text{-naphthalenediyl}$ ), which are retained on the clusters [2].



### 3. Experimental

#### 3.1. General experimental conditions

All reactions were carried out under dry, high purity argon using standard Schlenk techniques. Common solvents were dried, distilled under argon and degassed before use.

#### 3.2. Instrumentation

Infrared spectra were obtained on a Bruker IFS28 FT-IR spectrometer. Spectra in  $\text{CH}_2\text{Cl}_2$  were obtained using a 0.5 mm path-length solution cell with NaCl windows. NMR spectra were recorded on Bruker AM300WB ( $^1\text{H}$  at 300.13 MHz) or 600 Unity Nova ( $^1\text{H}$  at 599.92 MHz) instruments. Samples were dissolved in  $\text{CDCl}_3$ , unless otherwise stated, contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane. ES mass spectra: A VG Platform 2 instrument was used, solutions in MeOH being directly infused into the instrument. Chemical aids to ionisation were used as required [12]. Elemental analyses were performed at CMAS, Melbourne, Australia.

#### 3.3. Reagents

The ligand dmpn [13],  $\text{Ru}_3(\text{CO})_{12}$  [14] and  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$  [15] were made by the cited literature methods. ONMe<sub>3</sub> (tmno) was sublimed before use.

#### 3.4. Reaction of $\text{Ru}_3(\text{CO})_{12}$ with dmpn

To a solution of  $\text{Ru}_3(\text{CO})_{12}$  (106 mg, 0.166 mmol) in thf (20 ml) was added a solution of dmpn (40 mg, 0.161 mmol) in thf (4 ml); tmno (30 mg, 0.40 mmol) was then added as solid producing a colour change to deep red. After stirring for 1 h and evaporation to dryness, preparative t.l.c. (acetone–hexane 1/3) separated four major bands. Band 1 (red,  $R_f = 0.42$ ) contained  $\text{Ru}_3(\text{CO})_{10}(\text{dmpn})$  (**1**) (7.6 mg, 6%), obtained as red crystals from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ . Anal. Found: C, 34.72; H, 2.19%. Calc. ( $\text{C}_{24}\text{H}_{18}\text{O}_{10}\text{P}_2\text{Ru}_3$ ): C, 34.67; H, 2.18%;  $M$ , 833. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2073m, 2023vs, 1994vs (br), 1963m, 1930 (sh)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.88 [vt,  $J(\text{PH}) = 9.0$  Hz, 12H, 4  $\times$  Me], 7.59–7.62, 7.85–7.88, 7.99–8.01 (3  $\times$  2H, 3  $\times$  m, 6H, nap). ES-MS (positive ion, MeOH + NaOMe,  $m/z$ ): 856,  $[\text{M} + \text{Na}]^+$ ; 828,  $[\text{M} + \text{Na} - \text{CO}]^+$ . Band 2 (orange,  $R_f = 0.44$ ) contained  $\text{Ru}_3(\text{CO})_{10}\{\text{PMe}_2(\text{nap})\}_2$  (**3**) (2.6 mg, 2%), obtained as red crystals from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ . Anal. Found: C, 42.47; H, 2.81%. Calc. ( $\text{C}_{34}\text{H}_{26}\text{O}_{10}\text{P}_2\text{Ru}_3$ ): C, 42.55; H, 2.73%;  $M$ , 961. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2070w, 2015vs, 1993 (sh), 1991vs, 1988vs, 1970 (sh), 1957 (sh)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.04 [d,  $J(\text{HP}) = 8.4$  Hz, 12H,

4 × Me], 7.45–7.47, 7.51–7.57, 7.62–7.65, 7.90–7.92, 8.34–8.35 (5 × m, 14H, nap). EI-MS (positive ion, MeOH, *m/z*): 961, M<sup>+</sup>; (positive ion, MeOH + NaOMe): 984, [M + Na]<sup>+</sup>; (negative ion, MeOH + NaOMe): 992 [M + OMe]<sup>-</sup>. Band 3 (orange, *R<sub>f</sub>* = 0.60) contained Ru<sub>3</sub>(CO)<sub>11</sub>{PMe<sub>2</sub>(nap)} (2) (20.4 mg, 16%) obtained as an orange-red powder from CH<sub>2</sub>Cl<sub>2</sub>/MeOH. Anal. Found: C, 34.60; H, 1.67%. Calc. (C<sub>23</sub>H<sub>13</sub>O<sub>11</sub>PRu<sub>3</sub>): C, 34.55; H, 1.64%; *M*, 801. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2095w, 2043vs, 2026vs, 2011vs, 1984 (sh), 1954 (sh) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.13 [d, *J*(HP) 8.4 Hz, 6H, 2 × Me], 7.52–7.55, 7.57–7.64, 7.68–7.71, 7.98–7.99, 8.30–8.32 (m, 7H, nap). EI-MS (negative ion, MeOH + NaOMe, *m/z*): 832, [M + OMe]<sup>-</sup>; 804, [M + OMe – CO]<sup>-</sup>, 776, [M + OMe – 2CO]<sup>+</sup>. Band 4 (yellow, *R<sub>f</sub>* = 0.92) (16.0 mg, 15%) was identified as Ru<sub>3</sub>(CO)<sub>12</sub> by comparison of its IR ν(CO) spectrum with that of an authentic sample.

### 3.5. Reaction of Ru<sub>3</sub>(CO)<sub>10</sub>(μ-dppm) with dmpn

To a solution of Ru<sub>3</sub>(CO)<sub>10</sub>(μ-dppm) (200 mg, 0.207 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 ml) was added a solution of dmpn (65 mg, 0.26 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml). Tmno (38 mg, 0.40 mmol) was then added as solid producing a colour change from orange-red to dark red. After stirring for 2 h and evaporation to dryness, preparative t.l.c. (acetone–hexane 1/4) gave one major band (orange, *R<sub>f</sub>* = 0.55) which was extracted and crystallised (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to give Ru<sub>3</sub>(μ-dppm)(CO)<sub>9</sub>{PMe<sub>2</sub>(nap)} (4) (105 mg, 45%) as dark red crystals. Anal. Found: C, 49.03; H, 3.08%. Calc. (C<sub>46</sub>H<sub>35</sub>O<sub>9</sub>P<sub>3</sub>Ru<sub>3</sub>): C, 48.99; H, 3.13%; *M*, 1129. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2050w, 1989vs, 1972vs, 1936w(br) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 2.04 [d, *J*(HP) 8.4 Hz, 6H, 2 × Me], 4.21 [t, *J*(HP) 10.8 Hz, 2H, CH<sub>2</sub>], 7.34–7.39 (m, 20H, Ph), 7.48–7.51, 7.56–7.60, 7.65–7.68, 7.93–7.95, 8.43–8.45 (m, 7H, nap). EI-MS (positive ion, MeOH + NaOMe, *m/z*): 1152, [M + Na]<sup>+</sup>; 1129, M<sup>+</sup>; (negative ion, MeOH + NaOMe): 1128, [M – H]<sup>-</sup>; 940, [M – H – PMe<sub>2</sub>nap]<sup>-</sup>; 912, [M – H – PMe<sub>2</sub>nap – CO]<sup>-</sup>.

### 3.6. Pyrolysis of Ru<sub>3</sub>(CO)<sub>11</sub>{PMe<sub>2</sub>(nap)} (2)

A solution of Ru<sub>3</sub>(CO)<sub>11</sub>{PMe<sub>2</sub>(nap)} (49 mg, 0.061 mmol) in thf (12 ml) was refluxed for 18 h then evaporated to dryness. Preparative t.l.c. (acetone–hexane 1/2) gave a major band (orange, *R<sub>f</sub>* = 0.72) which was extracted and crystallised (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to give Ru<sub>3</sub>(μ-H)<sub>2</sub>(μ<sub>3</sub>-PMe<sub>2</sub>C<sub>10</sub>H<sub>5</sub>)(CO)<sub>8</sub> (5) (28 mg, 64%) as orange-yellow crystals. Anal. Found: C, 33.69; H, 2.21%. Calc. (C<sub>20</sub>H<sub>13</sub>O<sub>8</sub>PRu<sub>3</sub>): C, 33.57; H, 1.83%; *M*, 717. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2079s, 2045vs, 2035s, 2004s, 1999 (sh), 1983m cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ –19.09 [dd, *J*(HP) 32.1 Hz, *J*(HH) 1.2 Hz, 1H, Ru–H], –16.02 [dd, *J*(HP) 9.9 Hz, *J*(HH) 1.2 Hz, 1H, Ru–H],

1.96 [d, *J*(HP) 10.2 Hz, 3H, Me], 2.01 [d, *J*(HP) 9.6 Hz, 3H, Me], 7.43–7.45, 7.51–7.53, 7.74–7.77, 7.81–7.83, 8.06–8.07 (m, 5H, C<sub>10</sub>H<sub>5</sub>). EI-MS (negative ion MeOH + NaOMe, *m/z*): 748, [M + OMe]<sup>-</sup>; 717, M<sup>-</sup>.

### 3.7. Pyrolysis of Ru<sub>3</sub>(CO)<sub>9</sub>(μ-ppm){PMe<sub>2</sub>(nap)} (4)

A solution of Ru<sub>3</sub>(μ-dppm)(CO)<sub>9</sub>{PMe<sub>2</sub>(nap)} (43 mg, 0.038 mmol) in thf (12 ml) was heated at reflux point overnight then evaporated to dryness (rotary evaporator). Preparative TLC (acetone–hexane 1/2) showed one major orange band (*R<sub>f</sub>* = 0.50) which was extracted and crystallised (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) to give Ru<sub>3</sub>(μ-H)<sub>2</sub>(μ<sub>3</sub>-PMe<sub>2</sub>C<sub>10</sub>H<sub>5</sub>)(μ-dppm)(CO)<sub>6</sub> (6) (34 mg, 86%) as orange crystals. Anal. Found: C, 49.37; H, 3.24%. Calc. (C<sub>43</sub>H<sub>35</sub>O<sub>6</sub>P<sub>3</sub>Ru<sub>3</sub>): C, 49.48; H, 3.38%; *M*, 1045. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 2025w, 2000m, 1975vs, 1968 (sh), 1940w, 1917w cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ –19.08 (m, ~0.15H, Ru–H), –17.94 (m, ~0.85H, Ru–H), –15.53 (m, ~0.85H, Ru–H), –15.06 (m, ~0.15H, Ru–H), 1.60 [d, *J*(HP) 9.6 Hz, ~0.85 × 3H, Me], 1.71 [d, *J*(HP) 9.6 Hz, ~0.15 × 3H, Me], 1.91 [d, *J*(HP) 9.0 Hz, ~0.85 × 3H, Me], 1.97 [d, *J*(HP) 9.6 Hz, ~0.15 × 3H, Me], 4.19 (m, 1H, CH<sub>2</sub>), 4.68 (m, 1H, CH<sub>2</sub>), 6.55–8.25 (m, 25H, Ph + C<sub>10</sub>H<sub>5</sub>). EI-MS (positive ion, MeOH + NaOMe, *m/z*): 1068, [M + Na]<sup>+</sup>; 1045, M<sup>+</sup>; (negative ion, MeOH + NaOMe): 1044, [M – H]<sup>-</sup>.

### 3.8. Structure determinations

Full spheres of diffraction data to the indicated limits were measured at ca. 153 K using a Bruker AXS CCD area-detector instrument. *N*<sub>tot</sub> reflections were merged to *N* unique (*R*<sub>int</sub> quoted) after “empirical”/multiscan absorption correction (proprietary software), *N*<sub>o</sub> with *F* > 4σ(*F*) being used in the full matrix least squares refinement. All data were measured using monochromatic Mo Kα radiation, λ = 0.71073 Å. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub> being constrained at estimated values. Conventional residuals *R*, *R*<sub>w</sub> on |*F*| are given [weights: (σ<sup>2</sup>(*F*) + 0.000*n<sub>w</sub>F*<sup>2</sup>)<sup>-1</sup>]. Neutral atom complex scattering factors were used; computation used the XTAL 3.7 program system [16]. Pertinent results are given in the Figure (which shows non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and Tables 1 and 2.

### 3.9. Variata

5. (*x*, *y*, *z*, *U*<sub>iso</sub>)<sub>H</sub> were refined throughout.

6. The precision of the determination did not permit confident location of the core hydrogens and these were positioned according to the difference map and spectroscopic evidence.

#### 4. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 246355–246359 (complexes **1**, **3–6**, respectively). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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