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Bimetallic bridged dppb {dppb = $Ph_2P(CH_2)_4PPh_2$} complexes [{$MI_2(CO)_3(P(OR)_3)$}$_2$(μ-dppb)] (M = Mo, W): X-ray crystal structure of [{$MoI_2(CO)_3(P(O^iPr)_3)$}$_2$(μ-dppb)]

Paul K. Baker[a], *, Latifah Abdol Latif[a, b], Margaret M. Meehan[a], Sabrina Zanin[a], Michael G. B. Drew[c]

[a] *Department of Chemistry, University of Wales, Bangor, Gwynedd LL57 2UW, U.K.*
[b] *Centre for Foundation Studies in Science, University of Malaya, 50603, Kuala Lumpur, Malaysia*
[c] *Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, U.K.*

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Abstract

Reaction of [$MI_2(CO)_3(NCMe)_2$] with one equivalent of $P(OR)_3$ in CH_2Cl_2 at room temperature, followed by the *in situ* addition of half a molar equivalent of dppb {dppb = $Ph_2P(CH_2)_4PPh_2$} gave the bimetallic complexes [{$MI_2(CO)_3(P(OR)_3)$}$_2$(μ-dppb)] (M = Mo, W, R = Me, Et, ^{i}Pr, ^{n}Bu; for M = W only, R = Ph) (**1→9**) in good yield. The molybdenum complex [{$MoI_2(CO)_3(P(O^iPr)_3)$}$_2$(μ-dppb)] (**5**) was crystallographically characterised and has crystallographic C_2 symmetry. Each molybdenum has a capped octahedral environment with $P(O^iPr)_3$ in the capping position, three carbonyls in the capped face and the phosphorus from the bridging dppb ligand together with two iodines in the uncapped face. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Bimetallic phosphine-bridged; Molybdenum(II); Tungsten(II); crystal structure

1. Introduction

Bimetallic transition-metal complexes containing bridging phosphines such as dppm {dppm = $Ph_2P(CH_2)PPh_2$} have received considerable attention over the years; in particular by Shaw and co-workers [1–7]. Although the zero-valent six-coordinate bimetallic complexes [{$Mo(CO)_5$}$_2${μ-$Ph_2P(CH_2)_nPPh_2$}] (n = 2, 3) have been prepared [8] by the reaction of [$Mo(CO)_6$] with $ONMe_3$ in the presence of $Ph_2P(CH_2)_nPPh_2$, very little work has been carried out on bimetallic phosphine-bridged seven-coordinate complexes of molybdenum(II) and tungsten(II).

In 1986 [9], we described the synthesis of the highly versatile seven-coordinate complexes [$MI_2(CO)_3(NCMe)_2$] (M = Mo, W). The complexes [$MI_2(CO)_3(NCMe)_2$] have been shown to display a wide range of chemistry [10,11]. In 1991 [12], we described the preparation and characterisation of a series of phosphine-bridged seven-coordinate complexes [{$MI_2(CO)_3L$}$_2$(μ-L–L)] {M = Mo, W; L = PPh_3, $AsPh_3$, $SbPh_3$; L–L = $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 4); L–L = [Fe(η^5-$C_5H_4PPh_2)_2$]}. No X-ray crystal structures of these complexes were obtained. Very few phosphite seven-coordinate complexes of molybdenum(II) and tungsten(II) have been described; two crystallographically characterised examples are [$MoCl(SnBuCl_2)(CO)_2${$P(OMe)_3$}$_3$] [13] and [$WBr_2(CO)${$P(OMe)_3$}$_2$ {$Me_2AsC(CF_3){=}C(CF_3)$ $AsMe_2$}] [14]. Phosphite ligands often help to increase the solubility of complexes, and enable suitable single crystals to be grown for X-ray analysis. In this paper, we describe the synthesis of the bimetallic phosphine-bridged phosphite complexes [{$MI_2(CO)_3(P(OR)_3)$}$_2$(μ-dppb)] {dppb = $Ph_2P(CH_2)_4PPh_2$; M = Mo, W, R = Me, Et, ^{i}Pr, ^{n}Bu; for M = W only, R = Ph}, which has been crystallographically characterised for M = Mo, R = ^{i}Pr.

2. Experimental

All reactions described in this paper were carried out under an atmosphere of dry nitrogen using standard vacuum/Schlenk line techniques. The starting materials, [$MI_2(CO)_3(NCMe)_2$] (M = Mo, W) were prepared by the published method [9]. The solvents CH_2Cl_2 and diethyl

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* Corresponding author. Fax: +44-1248-37058.

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ether were dried and distilled before use. All chemicals were purchased from commercial sources.

Elemental analyses (C, H and N) were determined using a Carlo Erba Elemental Analyser MOD 1108 (using helium as a carrier gas). Infrared spectra were recorded as thin $CHCl_3$ films between NaCl plates on a Perkin-Elmer 1600 series FTIR spectrophotometer. ^1H (referenced to $SiMe_4$) and ^{31}P (referenced to 85% H_3PO_4) NMR spectra were recorded on a Bruker AC 250 NMR spectrometer.

2.1. *Preparations*

2.1.1. *$[\{MoI_2(CO)_3(P(OMe)_3)\}_2(\mu\text{-}dppb)]$ (**1**)*

To a solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.969 mmol) in CH_2Cl_2 (30 cm^3) was added $P(OMe)_3$ (0.120 g, 0.969 mmol) with continuous stirring under a stream of dry nitrogen. The dark brown solution immediately changed to yellowish green. After 1 min of stirring, dppb (0.207 g, 0.485 mmol) was added and the mixture was further stirred for 1 h. Filtration, and removal of most of the solvent *in vacuo*, followed by a dropwise addition of Et_2O gave a yellowish green complex. After cooling the mixture at −5°C for 72 h, the solid upon recrystallisation from CH_2Cl_2–Et_2O (80:20) yielded $[\{MoI_2(CO)_3(P(OMe)_3)\}_2(\mu\text{-dppb})]$ (**1**) (0.838 g, 56%).

Similar reactions of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar amount of $P(OR)_3$ in CH_2Cl_2, followed by an *in situ* reaction with half an equivalent of dppb gives the bimetallic complexes $[\{MI_2(CO)_3(P(OR)_3)\}_2(\mu\text{-dppb})]$ (M = Mo, W, R = Et, ^{i}Pr, ^{n}Bu; M = W only, R = Me, Ph) (**2**→**9**). Suitable single crystals for X-ray crystallography of $[\{MoI_2(CO)_3(P(O^iPr)_3)\}_2(\mu\text{-dppb})]$ (**5**) were grown by cooling a CH_2Cl_2:Et_2O 80:20 solution of (**5**) at −5°C for 72 h. See Table 1 for physical and analytical data.

2.2. *X-ray crystallography*

Crystals of $[\{MoI_2(CO)_3(P(O^iPr)_3)\}_2(\mu\text{-dppb})]$ (**5**) were grown as described in Section 2.1. Bond lengths and angles for the metal coordination spheres of **5** are given in Table 1. Crystal data for **5**: $C_{58}H_{80}I_4Mo_2O_{14}P_4$, $M = 1824.58$, Mo Kα radiation, monoclinic, space group C2/c, $a = 40.52(4)$, $b = 10.469(12)$, $c = 20.76(2)$ Å, $\beta = 93.63(1)°$, $U = 8786$ Å^3, $Z = 4$, dm = 1.379 Mg m^{-3}, $\mu = 1.809$ mm^{-1}, $F(000) = 3584$. 9671 reflections were collected of which 6140 were unique, R(int) = 0.0570. Data were collected using the MARresearch Image Plate System. The crystal was positioned at 70 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [15]. The structure was solved using direct methods with the Shelx86 program [16]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. There was one water solvent molecule for which the hydrogen atoms could not be located and were not included and one benzene solvent molecule with a crystallographic centre of symmetry. An empirical absorption correction was carried out using the DIFABS program [17]. The structure was then refined using Shelxl [18]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. The final R values were $R_1 = 0.0572$, and $wR_2 = 0.1104$ for 1959 data with $I > 2\sigma(I)$.

Table 1
Dimensions in the metal coordination sphere bond lengths (Å) and angles (°)

Mo(1)–C(200)	1.958 (19)
Mo(1)–C(300)	2.104 (16)
Mo(1)–C(100)	2.144 (19)
Mo(1)–P(4)	2.407 (5)
Mo(1)–P(3)	2.613 (5)
Mo(1)–I(1)	2.873 (3)
Mo(1)–I(2)	2.881 (3)
C(200)–Mo(1)–C(300)	112.4 (7)
C(200)–Mo(1)–C(100)	111.4 (7)
C(300)–Mo(1)–C(100)	112.3 (7)
C(200)–Mo(1)–P(4)	70.9 (6)
C(300)–Mo(1)–P(4)	74.5 (5)
C(100)–Mo(1)–P(4)	74.2 (5)
C(200)–Mo(1)–P(3)	77.3 (5)
C(300)–Mo(1)–P(3)	160.9 (5)
C(100)–Mo(1)–P(3)	76.9 (5)
P(4)–Mo(1)–P(3)	124.55 (16)
C(200)–Mo(1)–I(1)	160.5 (5)
C(300)–Mo(1)–I(1)	77.0 (5)
C(100)–Mo(1)–I(1)	78.4 (5)
P(4)–Mo(1)–I(1)	128.58 (16)
P(3)–Mo(1)–I(1)	89.11 (11)
C(200)–Mo(1)–I(2)	78.9 (5)
C(300)–Mo(1)–I(2)	73.8 (5)
C(100)–Mo(1)–I(2)	163.0 (5)
P(4)–Mo(1)–I(2)	122.67 (14)
P(3)–Mo(1)–I(2)	92.95 (13)
I(1)–Mo(1)–I(2)	88.01 (8)

3. Results and discussion

The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo, W) [9] were prepared by refluxing $[M(CO)_6]$ in NCMe to give *fac*-$[M(CO)_3(NCMe)_3]$ [19], followed by an *in situ* addition of one equivalent of I_2 at 0°C. Treatment of $[MI_2(CO)_3(NCMe)_2]$ with an equimolar amount of $P(OR)_3$ in CH_2Cl_2 at room temperature gave $[MI_2(CO)_3(NCMe)\{P(OR)_3\}]$, which react *in situ* with half an equivalent of dppb to give high yields of the bimetallic complexes $[\{MI_2(CO)_3(P(OR)_3)\}_2(\mu\text{-dppb})]$ (M = Mo, W; R = Me, Et, ^{i}Pr, ^{n}Bu; M = W, R = Ph) (**1**→**9**). Complexes **1**→**9** have been characterised by elemental analysis (C, H and N) (Table 2), IR, ^1H and ^{31}P NMR

Table 2
Physical and analytical data[a] for [$\{MI_2(CO)_3(P(OR)_3)\}_2(\mu$-dppb)] complexes

Complex	Yield (%)	Colour	C (%)	H (%)
1 [$\{MoI_2(CO)_3(P(OMe)_3)\}_2(\mu$-dppb)]	56	yellow/green	31.6 (31.1)	3.2 (3.0)
2 [$\{WI_2(CO)_3(P(OMe)_3)\}_2(\mu$-dppb)]	53	yellow	28.5 (28.0)	2.9 (2.7)
3 [$\{MoI_2(CO)_3(P(OEt)_3)\}_2(\mu$-dppb)]·$CH_2Cl_2$	61	green/brown	33.9 (34.0)	3.7 (3.6)
4 [$\{WI_2(CO)_3(P(OEt)_3)\}_2(\mu$-dppb)]	63	yellow/green	30.9 (30.7)	3.3 (3.2)
5 [$\{MoI_2(CO)_3(P(O^iPr)_3)\}_2(\mu$-dppb)]	78	brown	37.1 (36.5)	4.7 (4.1)
6 [$\{WI_2(CO)_3(P(O^iPr)_3)\}_2(\mu$-dppb)]	80	yellow	33.0 (33.1)	3.8 (3.7)
7 [$\{MoI_2(CO)_3(P(O^nBu)_3)\}_2(\mu$-dppb)]	51	green/yellow	39.0 (38.7)	4.8 (4.6)
8 [$\{WI_2(CO)_3(P(O^nBu)_3)\}_2(\mu$-dppb)]	81	yellow	35.7 (35.4)	4.3 (3.9)
9 [$\{WI_2(CO)_3(P(OPh)_3)\}_2(\mu$-dppb)]·$CH_2Cl_2$	60	yellow	39.5 (39.2)	3.1 (2.8)

[a] Calculated values in parentheses.

spectroscopy (Table 3Table 4), and for M = Mo, R = ^{i}Pr by X-ray crystallography. Complexes **3** and **9** were confirmed as CH_2Cl_2 solvates by repeated elemental analyses and ^{1}H NMR spectroscopy. The complexes are all very soluble in $CHCl_3$ and CH_2Cl_2, and reasonably soluble in diethyl ether. They are considerably more soluble than the closely related complexes [$\{MI_2(CO)_3L\}_2(\mu$-L–L)] {M = Mo, W; L = PPh_3, $AsPh_3$, $SbPh_3$; L–L = $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 4); L–L = [Fe(η^5-$C_5H_4PPh_2)_2$]} which have been previously described [12]. Complexes **1**→**9** are indefinitely stable in the solid state when stored under nitrogen, but decompose in solution when exposed to air.

The IR spectra of complexes **1**→**9** all show three carbonyl bands which suggests that the molybdenum centre has the same arrangement of ligands, this has been confirmed by growing suitable single crystals for X-ray analysis of [$\{MoI_2(CO)_3(P(O^iPr)_3)\}_2(\mu$-dppb)] (**5**). For example, the IR spectrum ($CHCl_3$) of the crystallographically characterised complex [$\{MoI_2(CO)_3(P(O^iPr_3)_2)\}_2(\mu$-dppb)] (**5**) showed three carbonyl bands at ν(CO) = 2033 (w), 1976 (s) and 1940 (s), which agrees the structure for **5** shown in Fig. 1. The complex has two identical molybdenum(II) centres bridged by a bis(diphenylphosphino)butane molecule, with three carbonyl ligands in a capped face in a capped octahedral structure. As expected all of the very similar new complexes **1**–**9** have three carbonyl stretching bands in their IR spectra with both similar patterns and stretching frequencies to each other. Suitable single crystals for X-ray crystallography were grown by cooling a CH_2Cl_2:Et_2O (80:20) solution of **5** at −5°C for 72 h.

The molecular structure of **5** is shown in Fig. 1, together with the atomic numbering scheme. The structure consist of discrete [$\{MoI_2(CO)_3(P(O^iPr)_3)\}_2(\mu$-dppb)] dinuclear units with crystallographically imposed C_2 sym-

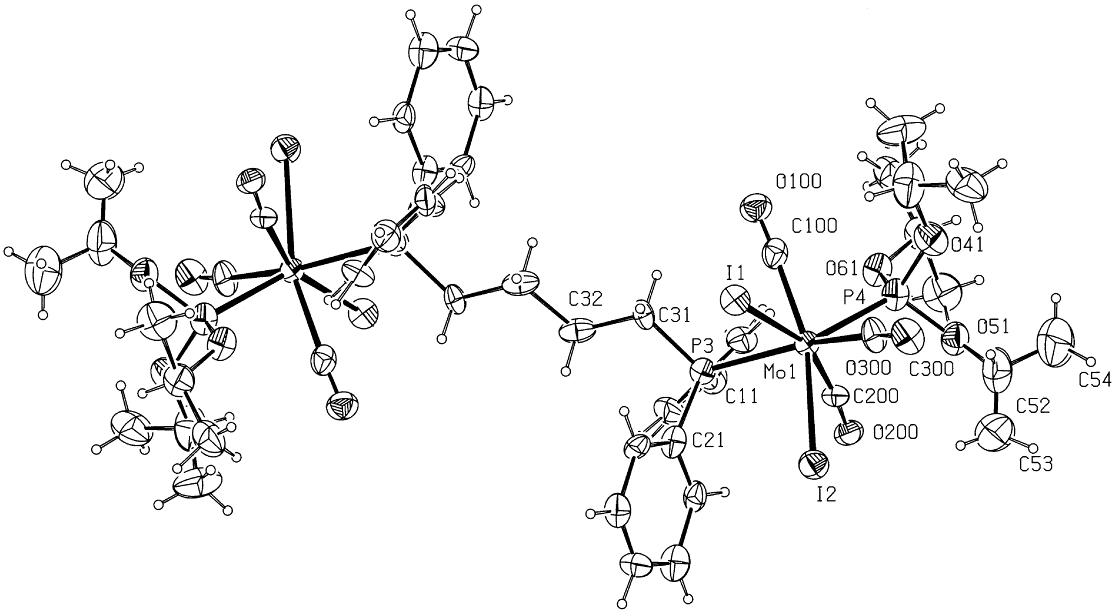

Fig. 1. The structure of [$\{MoI_2(CO)_3(P(O^iPr)_3)\}_2(\mu$-dppb)] (**5**) with ellipsoids at 30% probability.

Table 3
$^1\mathrm{H}$ NMR data (δ)[a] for the complexes $[\{\mathrm{MI_2(CO)_3(P(OR)_3)}\}_2(\mu\text{-dppb})]$

Complex	$^1\mathrm{H}$ (δ) (ppm)
1	7.6–7.4 {br, m, 20H, $\mathit{Ph}_2\mathrm{P(CH_2)_4P}\mathit{Ph}_2$}; 3.86 {d, 18H, $\mathrm{P(OC}\mathit{H}_3)_3$}; 3.0 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)PPh_2}$}; 1.5 {br, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}
2	7.6–7.4 {br, m, 20H, $\mathit{Ph}_2\mathrm{P(CH_2)_4P}\mathit{Ph}_2$}; 3.77 {d, 18H, $\mathrm{P(OCH_3)_3}$}; 3.0 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)PPh_2}$}; 1.4 {br, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}
3	7.6–7.4 {br, m, 20H, $\mathit{Ph}_2\mathrm{P(CH_2)_4P}\mathit{Ph}_2$}; 5.3 (s, 2H, $\mathrm{C}\mathit{H}_2\mathrm{Cl_2}$); 4.2 {m, 12H, $\mathrm{P(OC}\mathit{H}_2\mathrm{)CH_3)_3}$}; 3.0 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)PPh_2}$}; 1.5 {br, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}; 1.4 {t, 18H, $\mathrm{P(OCH_2C}\mathit{H}_3)_3$}
4	7.6–7.3 {br, m, 20H, $\mathit{Ph}_2\mathrm{P(CH_2)_4P}\mathit{Ph}_2$}; 4.25 {q, 12H, $\mathrm{P(OC}\mathit{H}_2\mathrm{CH_3)_3}$}; 3.1 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)PPh_2}$}; 1.5 {br, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}; 1.4 {t, 18H, $\mathrm{P(OCH_2C}\mathit{H}_3)_3$}
5	7.6–7.2 {br, m, 20H, $\mathit{Ph}_2\mathrm{P(CH_2)_4P}\mathit{Ph}_2$}; 4.72 {m, 6H, $\mathrm{P(OC}\mathit{H}\mathrm{(CH_3)_2}$}; 3.0 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)_4PPh_2}$}; 1.5 {br, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}; 1.38 {d, 36H, $\mathrm{P(OCH(C}\mathit{H}_3)_2)_3$}
6	7.5–7.3 {br, m, 20H, $\mathit{Ph}_2\mathrm{P(CH_2)_4P}\mathit{Ph}_2$}; 4.7 {m, 6H, $\mathrm{P(OC}\mathit{H}\mathrm{(CH_3)_2)_3}$}; 3.0 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)PPh_2}$}; 1.4 {br, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}; 1.36 {d, 36H, $\mathrm{P(OCH(C}\mathit{H}_3)_2)_3$}
7	7.5–7.4 {br, 20H, $\mathit{Ph}_2\mathrm{P(CH_2)_4P}\mathit{Ph}_2$}; 4.15 {m, 12H, $\mathrm{P(OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3)_3}$}; 3.0 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)PPh_2}$}; 1.75 {m, 12H, $\mathrm{P(OCH_2C}\mathit{H}_2\mathrm{CH_2CH_3)_3}$}; 1.45 {m, 12H, $\mathrm{P(OCH_2CH_2C}\mathit{H}_2\mathrm{CH_3)_3}$}; {m, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}; 1.0 (t, 18H, $\mathrm{P(OCH_2CH_2CH_2C}\mathit{H}_3)_3$)
8	7.5–7.4 {br, 20H, $\mathit{Ph}_2\mathrm{P(CH_2)_4P}\mathit{Ph}_2$}; 4.05 {m, 12H, $\mathrm{P(OC}\mathit{H}_2\mathrm{CH_2CH_2CH_3)_3}$}; 3.0 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)PPh_2}$}; 1.75 {m, 12H, $\mathrm{P(OCH_2C}\mathit{H}_2\mathrm{CH_2CH_3)_3}$}; 1.45 {m, 12H, $\mathrm{P(OCH_2CH_2C}\mathit{H}_2\mathrm{CH_3)_3}$}; {m, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}; 0.95 {t, 18H, $\mathrm{P(OCH_2CH_2CH_2C}\mathit{H}_3)_3$}
9	7.6–7.0 (br, m, 50H, Ph); 5.3 (s, 2H, $\mathrm{C}\mathit{H}_2\mathrm{Cl_2}$); 3.1 {br, 4H, $\mathrm{Ph_2P(C}\mathit{H}_2\mathrm{CH_2CH_2C}\mathit{H}_2\mathrm{)PPh_2}$}; 1.35 {br, 4H, $\mathrm{Ph_2P(CH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2)PPh_2}$}

[a] Spectra recorded in $\mathrm{CDCl_3}$ (+25°C) and referenced to $\mathrm{SiMe_4}$; br = broad; s = singlet, d = doublet, m = multiplet, t = triplet.

Table 4
$^{31}P-\{^1H\}$ NMR data (δ)[a] for the complexes $[\{MI_2(CO)_3(P(OR)_3)\}_2(\mu\text{-dppb})]$

Complex	^{31}P (δ)(ppm)/J(Hz)
1	171.83 {d, $P(OMe)_3$}; 6.09 {d, $Ph_2P(CH_2)_4PPh_2$}; $J_{WP}=312$
2	136.36 {br, $P(OMe)_3$}; $J_{WP}=216$; -16.41 {br, $Ph_2P(CH_2)_4PPh_2$}; $J_{WP}=361$
3	163.70 {br, $P(OEt)_3$}; 6.90 {d, $Ph_2P(CH_2)_4PPh_2$}, $^2J_{PP}=24.8$
4	127.82 {br, $P(OEt)_3$}; -15.53 {br, $Ph_2P(CH_2)_4PPh_2$}
5	156.42 {d, $P(O^iPr)_3$}, $^2J_{PP}=25.4$; 7.33 {d, $Ph_2P(CH_2)_4PPh_2$}
6	119.61 {d, $P(O^iPr)_3$}, $J_{WP}=220$, $^2J_{PP}=24.4$; -15.18 {d, $Ph_2P(CH_2)_4PPh_2$}, $J_{WP}=147$
7	163.75 {br, $P(O^nBu)_3$}; 7.03 {d, $Ph_2P(CH_2)_4PPh_2$}, $^2J_{PP}=24.4$
8	127.65 {br, $P(O^nBu_3)$}, $J_{WP}=289$; -15.32 {br, $Ph_2P(CH_2)_4PPh_2$}
9	126.30 {br, $P(OPh)_3$}; -17.72 {br, $Ph_2P(CH_2)_4PPh_2$}

[a] Spectra recorded in $CDCl_3$ (+25°C) and referenced to 85% H_3PO_4; br = broad, d = doublet.

metry. As is apparent in Fig. 1, the butane link is consistently *trans*. The environment of each molybdenum atom (dimensions given in Table 1) is capped octahedral with the phosphite in the capped position (Mo–P 2.407(5) Å), three carbonyls in the capped face (1.96(2), −2.14(2) Å) and the phosphorus from the bridging dppb ligand in the uncapped face (Mo–P(4) 2.613(5) Å), together with two iodides (Mo–I(1) 2.873(3), Mo–I(2) 2.881(3) Å).

The ^1H and ^{31}P NMR spectra for **1**→**9** also suggest the presence of a single isomer in solution, and conform with structure for **5** shown in Fig. 1. The ^1H NMR data Table 3, have as expected all the ligand proton resonances slightly shifted downfield compared to the uncoordinated ligands. The symmetrical nature of the bridging dppb ligand is also confirmed in the ^1H NMR spectra of **1**–**9**, all of which show the CH_2 groups next to the phosphorus atoms to be equivalent and the inner pair of CH_2 groups are also found to be equivalent. The $^{31}P\{^1H\}$ NMR spectra of **1**–**9** Table 4 also agree with the symmetrical structure of complex **5**. For example, the crystallographically characterised complex **5** has two resonances in its ^{31}P NMR spectrum. One at $\delta=156.42$ ppm due to the equivalent phosphite ligands, which is split into a doublet by the equivalent PPh_2 groups on the dppb ligand, with a coupling constant of $^2J_{PP}=25.4$ Hz. Similarly, the resonance for **5** at $\delta=7.33$ ppm due to the equivalent PPh_2 groups on the dppb ligand, also a doublet with an identical coupling constant. In summary, the IR, ^1H and ^{31}P NMR data confirms the symmetrical structure as shown for complex **5**, and it is very likely that complexes **1**–**4** and **6**–**9** have similar structures to complex **5**. We are currently exploring the catalytic activity of **1**→**9** as alkene metathesis catalysts.

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References

[1] Blagg A, Hutton AT, Pringle PG, Shaw BL. J. Chem. Soc. Dalton Trans. 1984;1815.

[2] Hassan FSM, Markham DP, Pringle PG, Shaw BL. J. Chem. Soc. Dalton Trans. 1985;279.

[3] Iggo JA, Shaw BL. J. Chem. Soc. Dalton Trans. 1985;1009.

[4] Blagg A, Shaw BL. J. Chem. Soc. Dalton Trans. 1987;221.

[5] Blagg A, Shaw BL, Thornton-Pett M. J. Chem. Soc. Dalton Trans. 1987;769.

[6] Jacobsen GB, Shaw BL, Thornton-Pett M. J. Chem. Soc. Dalton Trans. 1987;1509.

[7] Blagg A, Robson R, Shaw BL, Thornton-Pett M. J. Chem. Soc. Dalton Trans. 1987;2171.

[8] Hor TSA. J. Organomet. Chem. 1987;319:213.

[9] Baker PK, Fraser SG, Keys EM. J. Organomet. Chem. 1986;309:319.

[10] Baker PK. Adv. Organomet. Chem. 1996;40:45 and references cited therein.

[11] Baker PK. Chem. Soc. Rev. 1998;27:125 and references cited therein.

[12] Baker PK, van Kampen M, ap Kendrick D. J. Organomet. Chem. 1991;421:241.

[13] Miguel D, Pérez-Martínez Riera V, Garcia-Granda S. J. Organomet. Chem. 1993;455:121.

[14] Mihichuk L, Pizzey M, Robertson B, Barton R. Can. J. Chem. 1986;64:991.

[15] Kabsch W. J. Appl. Cryst. 1988;21:916.

[16] Sheldrick GM. Shelx86. Acta Cryst. A 1990;46:467.

[17] Walker N, Stuart D. Acta Cryst. A 1983;39:158.

[18] Sheldrick GM. Shelxl, Program for Crystal Structure Refinement, University of Göttingen, 1993.

[19] Tate DP, Knipple WR, Augl JM. Inorg. Chem. 1962;1:433.