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Synthesis and molecular structures of dinuclear complexes with 1,2-dihydro-1,2-diphenyl-naphtho[1,8-c,d]1,2-diphosphole as a bridging ligand

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Abstract

A bisphosphine in which a PhP–PPh bond bridges 1,8-positions of naphthalene, 1,2-dihydro-1,2-diphenyl-naphtho[1,8-cd]-1,2-diphosphole (**1**), was used as a bridging ligand for the preparation of dinuclear group 6 metal complexes. Free *trans*-**1**, a more stable isomer having two phenyl groups on phosphorus centers mutually *trans* with respect to a naphthalene plane, was allowed to react with two equivalents of $M(CO)_5(thf)$ (M = W, Mo, Cr) at room temperature to give dinuclear complexes $(OC)_5M(\mu\text{-}trans\text{-}\mathbf{1})M(CO)_5$ (M = W (**2a**), Mo (**2b**), Cr (**2c**)). The preparation of the corresponding dinuclear complexes bridged by the *cis* isomer of **1** was also carried out starting from the free *trans*-**1** in the following way. Mono-nuclear complexes $M(trans\text{-}\mathbf{1})(CO)_5$ (M = W (**3a**), Mo (**3b**), Cr (**3c**)) which had been prepared by a reaction of *trans*-**1** with one equivalent of the corresponding $M(CO)_5(thf)$ (M = W, Mo, Cr) complex, were heated in toluene, wherein a part of the *trans*-**3a**–**c** was converted to their respective *cis* isomer $M(cis\text{-}\mathbf{1})(CO)_5$. Each *cis trans* mixture of the mono-nuclear complexes **3a**–**c** was treated with the corresponding $M(CO)_5(thf)$ to give a *cis trans* mixture of the respective dinuclear complexes **2a**–**c**. The *cis* isomer of the ditungsten complex **2a** was isolated, and its molecular structure was confirmed by X-ray analysis, showing a shorter W···W distance of 5.1661(3) Å than that of 5.8317(2) Å in *trans*-**2a**.

Keywords: Bisphosphine; Dinuclear complex; Tungsten; Molybdenum; Chromium

1. Introduction

The chemistry of dinuclear complexes is rapidly growing, which has been brought about by significant progress in a synthetic methodology. The most successful approach to the synthesis of dinuclear complexes is to use a bridging ligand [1]. Phosphido groups, R_2P^-(Fig. 1(a)), and bis(diorganophosphino)methanes, $R_2PCH_2PR_2$ (Fig. 1(b)), have been widely used as a bridging ligand because of their ability to form a stable phosphorus-metal bond with a variety of metal fragments [2,3]. In these dinuclear complexes, the two metal centers in close proximity have a potential to facilitate the simultaneous or consecutive activation and transformation of substrate molecules.

Bisphosphines, $R_2P–PR_2$, are also a promising ligand which can lock together two metal centers in close proximity as shown in Fig. 1(c). Since early 1960s, bisphosphines have been used for syntheses of a variety of dinuclear complexes [4,5]. However, such examples are considerably smaller in number than the dinuclear complexes having the R_2P^- and/or $R_2PCH_2PR_2$ ligands as the bridge(s). The slow progress concerning the $R_2P–PR_2$-bridged dinuclear complexes is partly due to a relatively weak P–P bond of the bisphosphine ligand.

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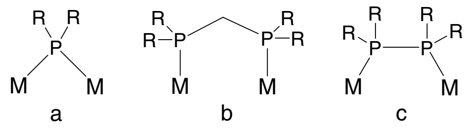
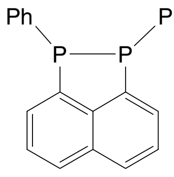


Fig. 1. Phosphorus-based bridging ligands which can lock together two metal centers in close proximity.

Recently, our group reported a novel bisphosphine ligand **1**, in which two phosphorus atoms are locked with a robust naphthalene group [6], rendering the phosphorus–phosphorus bond fairly stable. Here we report, the synthesis of dinuclear complexes bridged by the robust phosphorus–phosphorus bond.



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2. Results and discussion

1,2-dihydro-1,2-diphenyl-naphtho[1,8-cd]-1,2-diphosphole, **1**, was prepared from dilithionaphthalene and dichlorophenylphosphine [6,7]. The molecular structure determined by X-ray analysis is shown in Fig. 2 [8], where two phenyl groups on the phosphorus atoms adopt a mutually *trans* disposition with respect to a naphthalene plane. The ligand **1** (*trans*-**1**) reacts with two equivalents of M(CO)$_5$(thf) (M = W, Mo, Cr) at room temperature to give an expected product, (OC)$_5$M(μ-*trans*-**1**)M(CO)$_5$ (M = W (**2a**), Mo (**2b**), Cr (**2c**)) in almost quantitative yields. ^{31}P{^{1}H} NMR spectra of these complexes show a singlet at 30.4 ppm with satellites due to ^{183}W($I = 1/2$, $^{1}J_{PW} = 166$ Hz, $^{2}J_{PW} = 81$ Hz) for the tungsten complex **2a**, and a singlet at 49.1 and 71.7 ppm for the molybdenum and chromium complexes, **2b** and **2c**, respectively. For the tungsten complex **2a**, the molecular structure was confirmed by the X-ray analysis. An ORTEP drawing is shown in Fig. 3, where *trans*-**1** bridges the two W(CO)$_5$ fragments. A P1–P2 distance of **2a** is 2.270(1) Å which is slightly longer than 2.2240(6) and 2.2246(6) Å for those of two independent molecules in the crystal of *trans*-**1**. The P1–P2 bond of **2a** in Fig. 3 is twisted by 15.7° with respect to the naphthalene plane, whereas the P1–P2 bond of free *trans*-**1** in Fig. 2 is almost parallel to the plane. The reason for the deformation is not clear at present. Each of the two phosphorus centers P1 and P2 in Fig. 3 forms a tetrahedral geometry with usual W–P distances, 2.5335(9) and 2.5224(9) Å for W1–P1 and W2–P2, respectively. A separation between the two tungsten centers amounts to 5.8317(2) Å, which is significantly longer than 3–4 Å found in the R$_2$P$^-$- and/or R$_2$PCH$_2$PR$_2$-bridged complexes shown in Fig. 4 [9,10]. Since the *trans* disposition of the two tungsten fragments makes their separation large, synthesis of the *cis* isomer was attempted.

The *cis* isomer of **2**, (OC)$_5$M(μ-*cis*-**1**)M(CO)$_5$, would be obtained, if free *cis*-**1** were used in place of *trans*-**1**.

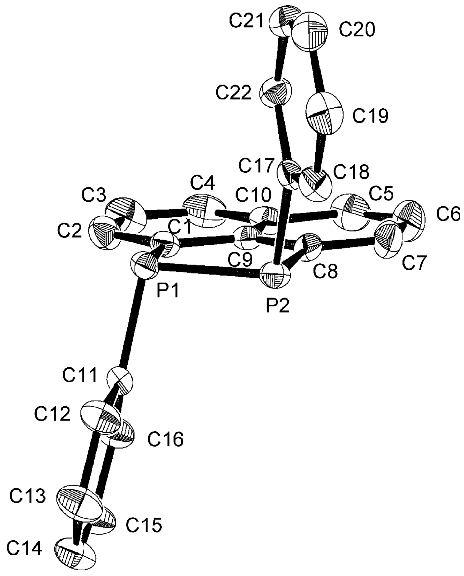

Fig. 2. An ORTEP drawing of **1** with 50% thermal ellipsoids. This is for one of the two independent molecules found in the crystal **1**. The selected bond distances (Å) and angles (°) are P1–P2 2.2240(6), P1–C1 1.830(2), P1–C11 1.841(2), P2–C8 1.838(2), P2–C17 1.837(2), P2–P1–C1 93.83(5), P2–P1–C11 98.90(5), C1–P1–C11 102.40(7), P1–P2–C8 93.19(5), P1–P2–C17 101.50(5), C8–P2–C17 103.81(7).

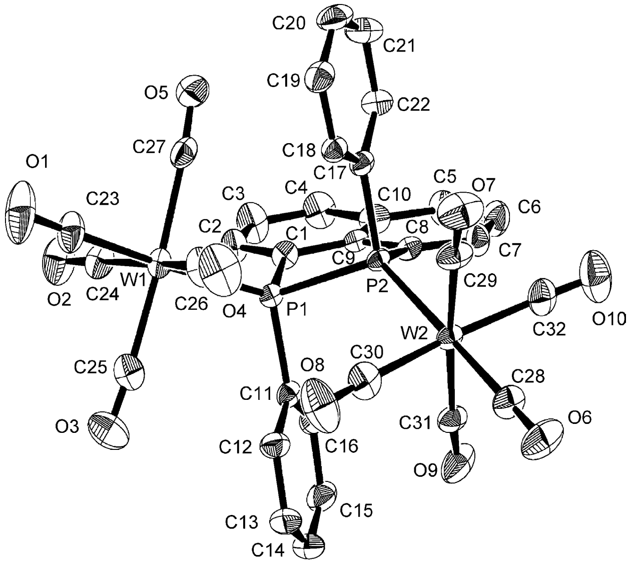

Fig. 3. An ORTEP drawing of (OC)$_5$W(μ-*trans*-**1**)W(CO)$_5$ (*trans*-**2a**) with 50% thermal ellipsoids. The selected bond distances (Å) and angles (°) are W1–P1 2.5335(9), W2–P2 2.5224(9), P1–P2 2.270(1), P1–C1 1.819(4), P1–C11 1.837(4), P2–C8 1.828(4), P2–C17 1.833(4), W1–P1–P2 123.54(4), W2–P2–P1 122.28(4), P2–P1–C1 92.3(1), P2–P1–C11 99.4(1), C1–P1–C11 101.6(2), P1–P2–C8 91.6(1), P1–P2–C17 101.3(1), C8–P2–C17 101.7(2).

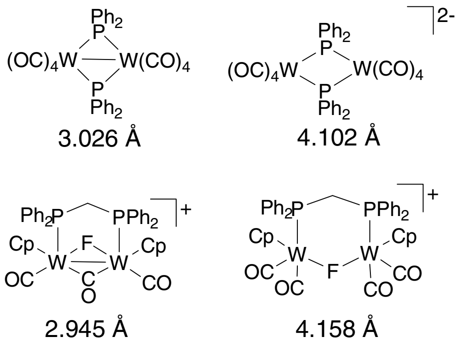

Fig. 4. Tungsten–tungsten distances for some dinuclear tungsten complexes bridged by Ph_2P^- or $Ph_2PCH_2PPh_2$ groups.

The *cis* configuration of the free ligand **1** is attained in principle through the inversion of configuration at a phosphorus center of *trans*-**1**. Since the inversion barrier has been estimated to be ca. 25 kcal/mol for the bisphosphines, which is lower by ca. 10 kcal/mol than for the usual mono phosphines [11,12], heating of free *trans*-**1** in toluene was carried out with an expectation of the inversion of the configuration. After heating overnight at 80 °C, $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated that a trace of a new signal appeared at −19.7 ppm which is probably assigned to *cis*-**1**. However, the new signal did not increase in intensity any more by prolonged heating, indicating that the *cis*–*trans* isomerization has reached to a thermal equilibrium. The relative instability of *cis*-**1** is mainly due to a steric repulsion between the two phenyl groups disposed at the same side with respect to the naphthalene plane. In addition, a repulsive interaction is also expected between two lone pairs on the phosphorus atoms of *cis*-**1**, although it is reported to be faint owing to a significant s character of the lone pair on the phosphorus [13,14]. Such steric and lone pair repulsions are absent in *trans*-**1**, as is evident in Fig. 2.

Here, assuming that a bulky fragment is introduced to one of the two phosphorus atoms of free *trans*-**1**, the introduced fragment exerts a steric repulsion on the phenyl group at the vicinal phosphorus center as depicted in Fig. 5(a). On the other hand, for a corresponding *cis* isomer, the bulky fragment does not make any repulsion against the phenyl group on the vicinal center, although the Ph–Ph repulsion is originally present as shown in Fig. 5(b). Thus, the additional steric repulsion introduced in Fig. 5(a) will reduce the relative stability of the *trans* isomer. In addition, the fragment introduced to the *cis* isomer eliminates the lone pair repulsion which was partly responsible for the relative instability of free *cis*-**1**. Consequently, the thermal equilibrium is expected to be shifted to some extent toward the *cis* isomer. Such a situation will be accomplished by the introduction of only one bulky metal fragment such as $M(CO)_5$ to the free ligand **1**.

A reaction of *trans*-**1** with one equivalent of $M(CO)_5(thf)$ (M = W, Mo, Cr) at room temperature gave M(*trans*-**1**)$(CO)_5$ (M = W (**3a**), Mo (**3b**), Cr (**3c**)). $^{31}P\{^1H\}$ NMR spectra of these complexes exhibit two doublets. The phosphorus atoms coordinating to the metal center were observed at 13.1, 33.7 and 52.0 ppm for *trans*-**3a**–**c**, respectively, whereas non-coordinating ones were observed at −8.8, −8.5, and −8.1 ppm, respectively, which are in accord with −8.2 ppm for free *trans*-**1**. For the tungsten complex *trans*-**3a**, its structure was confirmed by the X-ray analysis as shown in Fig. 6, where one $W(CO)_5$ fragment is attached to *trans*-**1**. A noteworthy point is that a carbonyl group C24–O2 of the $W(CO)_5$ fragment is directed to the phenyl group on the neighboring phosphorus center. Judging from a distance of 3.001(3) Å between O2 and a mean plane of the phenyl group, the $W(CO)_5$ fragment apparently exerts a steric repulsion on the phenyl group as expect-

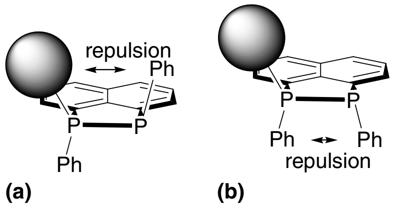

Fig. 5. A schematic representation of steric repulsions: (a) between a Ph group and a bulky fragment in the *trans* form; (b) between the two phenyl groups in the *cis* form.

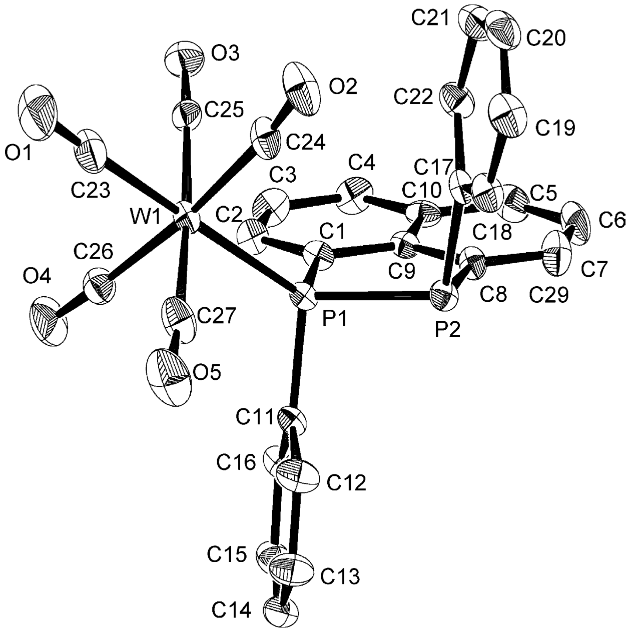

Fig. 6. An ORTEP drawing of W(*trans*-**1**)$(CO)_5$ (*trans*-**3a**) with 50% thermal ellipsoids. The selected bond distances (Å) and angles (°) are W1–P1 2.5242(6), P1–P2 2.2409(8), P1–C1 1.826(2), P1–C11 1.841(2), P2–C8 1.832(2), P2–C17 1.836(2), W1–P1–P2 125.70(3), P2–P1–C1 94.99(8), P2–P1–C11 97.10(7), C1–P1–C11 103.3(1), P1–P2–C8 91.66(8), P1–P2–C17 104.95(7), C8–P2–C17 101.2(1).

ed. The P2–P1–W1 angle, as a result, opens up to 125.70(3)°, and a P1–P2–C17(Ph) angle of 104.95(7)° is greater than 98.10(7)° and 101.50(7)° for the P–P–Ph angles of free *trans*-**1**.

The mono-nuclear *trans*-**3a**–**c** species thus obtained were heated in toluene. The $^{31}P\{^1H\}$ NMR spectra of the reaction mixture are shown for *trans*-**3a** in Fig. 7, which indicates that new two doublets coupled with each other appear at −1.7 and 2.7 ppm ($^1J_{P–P} = 238$ Hz). The new signal at 2.7 ppm is assigned to the phosphorus center bonding to the $W(CO)_5$ fragment, because it accompanies satellites due to ^{183}W. Unfortunately, separation of this species from *trans*-**3a** was not successful, but following results (vide infra) clearly indicate that this species is *cis*-**3a**. Similar thermal *trans*–*cis* conversion was carried out for the molybdenum and chromium analogs, *trans*-**3b** and **-3c**. In the $^{31}P\{^1H\}$ NMR spectra, new doublets were observed at −6.6 and 23.2 ppm ($^1J_{P–P} = 243$ Hz) for the former complex and at −9.7 and 47.3 ppm ($^1J_{P–P} = 253$ Hz) for the latter. The relative intensities of *trans* to *cis* isomers were similar to that of **3a**.

The *cis*–*trans* mixtures of **3** were then allowed to react with another equivalent of the corresponding metal fragment, $M(CO)_5(thf)$ (M = W, Mo, Cr). The $^{31}P\{^1H\}$ NMR spectra of the products show that, in addition to the signals at 29.9, 49.1, and 71.7 ppm due to *trans*-**2a**–**c**, respectively, new singlets were observed at 29.4, 46.5, and 68.0 ppm, respectively. For the tungsten case, we managed to isolate the new species having a signal at 29.4 ppm by means of a preparative scale HPLC over 30 times of recycling, and characterized as *cis*-**2a** by the X-ray analysis as shown in Fig. 8. It is highly probable that the *cis*-**2a** isomer is formed by the simple reaction of the $W(CO)_5$ with the *cis* isomer of **3a**. Thus, the new two doublets in Fig. 7 should be assigned to *cis*-**3a**. The molecular structure of *cis*-**2a** in Fig. 8 indicates that the two phenyl groups adopt a stacking form to minimize a steric congestion between them. However, judging from a short separation between these two phenyl planes, the steric repulsion is conceivable between them as for the free *cis* ligand. For example, *ipso* carbon atoms of the phenyl groups, C11 and C17, face a mean plane of their respective counterpart with distances of 2.88(1) and 2.91(1) Å, respectively, which are significantly smaller than the van der Waals contact distance of 3.40 Å.

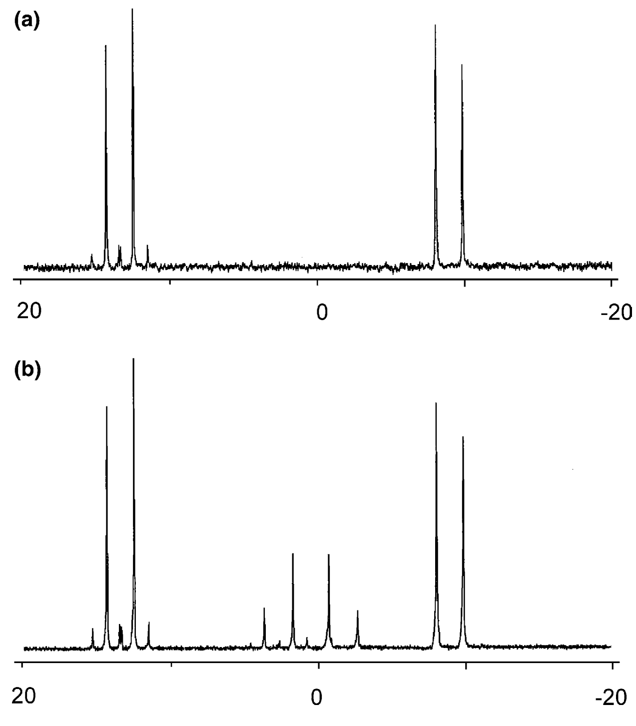

Fig. 7. $^{31}P\{^1H\}$ NMR spectra of **3a** in toluene: (a) before heating; (b) after heating.

The two bulky tungsten fragments in Fig. 8 are separated by 5.1661(3) Å, which is shorter than 5.8317(2) Å of *trans*-**2a** as expected, but it is still considerably longer than those of the complexes shown in Fig. 4. The reason for the fairly large W···W separation in *cis*-**2a** is that the carbonyl group C25–O3 on the W1 center are already in touch with the two carbonyl groups C29–O7 and C32–O10 on the W2 center, as is evident in the distances between these carbonyl groups, for example, O3···C29, 3.082(9) Å ; O3···C32, 3.044(10) Å. It seems crucial to reduce the steric bulkiness of the two metal fragments

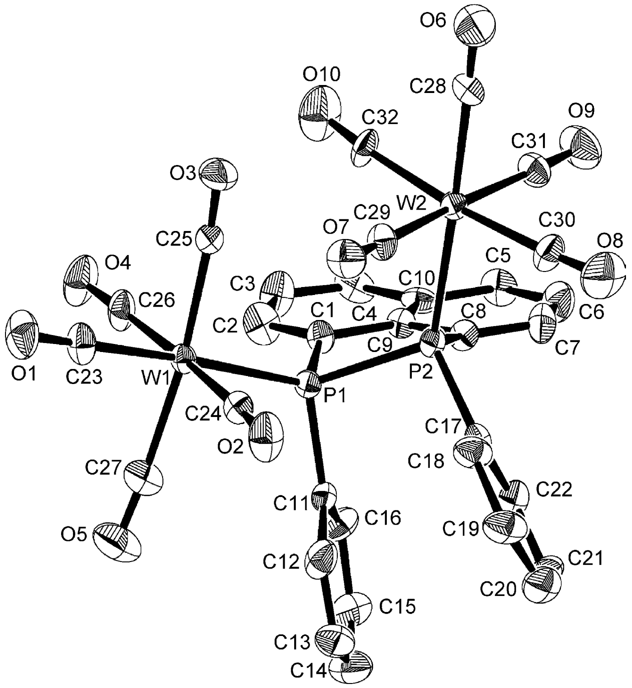

Fig. 8. An ORTEP drawing of $(OC)_5W(\mu\text{-}cis\text{-}\mathbf{1})W(CO)_5$ (*cis*-**2a**) with 50% thermal ellipsoids. The selected bond distances (Å) and angles (°) are W1–P1 2.535(1), W2–P2 2.514(2), P1–P2 2.280(2), P1–C1 1.817(6), P1–C11 1.841(6), P2–C8 1.825(6), P2–C17 1.842(7), W1–P1–P2 124.11(7), W2–P2–P1 120.90(7), P2–P1–C1 91.3(2), P2–P1–C11 101.5(2), C1–P1–C11 100.8(3), P1–P2–C8 91.2(2), P1–P2–C17 103.9(2), C8–P2–C17 106.3(3).

in order to let them come closer. Such an attempt is now under way.

3. Experimental

3.1. General remarks

All reactions were carried out under an atmosphere of dry nitrogen using Schlenk tube techniques. THF was distilled from sodium/benzophenone and toluene was distilled from sodium metal. These purified solvents were stored under an N_2 atmosphere. $CHCl_3$ and other reagents were used as received. *Trans*-**1** was prepared according to previously described methods [6].

IR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer. NMR spectra were recorded on a JEOL LA-300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were reported relative to Me_4Si and were determined by reference to the residual solvent peaks. ^{31}P NMR chemical shifts were reported relative to H_3PO_4 (85%) used as an external reference. Elemental analyses were performed with a Perkin–Elmer 2400CHN elemental analyzer.

Photolysis was carried out with Pyrex-glass-filtered emission from a 400 W mercury arc lamp (Riko-Kagaku Sangyo UVL-400P). The used emission-lines (nm) and their relative intensities (in parenthesis) were as follows: 577.0 (69), 546.1 (82), 435.8 (69), 404.7 (42), 365.0 (100), 334.1 (7), 312.6 (38), and 302.2 (9). Preparative-scale GPC was performed with a recycling HPLC system (Japan Analytical Industry Model LC-908) with JAIGEL-1H (20 mm ID×600 mm; exclusion limit: 1.0×10^{3}) and −2H (20 mm ID×600 mm; exclusion limit: 5.0×10^{3}) columns.

3.2. Synthesis of $(OC)_5W(\mu$-*trans*-**1**$)W(CO)_5$ (**2a**)

$W(CO)_6$ (510 mg, 1.4 mmol) dissolved in THF (40 mL) was irradiated by a mercury lamp for 2.5 h to generate $W(CO)_5$(thf) in situ. To a $W(CO)_5$(thf) solution thus obtained was added **1** (174 mg, 0.51 mmol) dissolved in a minimum amount of THF. The solution was stirred overnight, and THF was removed in vacuo. The residue was dissolved in $CHCl_3$ and passed through a short silica gel column (2 cm ID×2 cm). Since the product was contaminated with unreacted $W(CO)_6$ which was difficult to remove by a standard column technique, the product was purified by a preparative scale GPC column. **2a** was obtained almost quantitatively. Anal. Calcd for $C_{32}H_{16}O_{10}P_2W_2$: C, 38.82; H, 1.63. Found: C, 38.94; H, 1.61. IR (ν_{CO}, cm^{-1}, in THF): 2070, 1950. ^{1}H NMR (δ, in $CDCl_3$): 7.25–7.45 (m, 10H, Ph), 7.85 (t, $J_{HH}=7.1$ Hz, $J_{PH}=6.9$ Hz, 2H, 2,7-naph), 8.01 (m, 2H, 3,5-naph), 8.17 (d, $J_{HH}=8.2$ Hz, 2H, 4,5-naph). $^{13}C\{^{1}H\}$ NMR (δ, in $CDCl_3$): 128.1 (t, $J_{PC}=5.0$ Hz), 129.1 (t, $J_{PC}=4.0$ Hz), 130.7 (s), 131.5 (s), 133.1 (t, $J_{PC}=5.0$ Hz), 133.5 (t, $J_{PC}=7.6$ Hz), 133.7 (t, $J_{PC}=8.1$ Hz), 135.3 (t, $J_{PC}=18.3$ Hz), 136.9 (t, $J_{PC}=15.6$ Hz), 138.7 (t, $J_{PC}=5.6$ Hz), 195.7 (t, $J_{PC}=2.8$ Hz, $J_{CW}=126$ Hz, *cis*-CO), 197.3 (t, $J_{PC}=13.7$ Hz, *trans*-CO). $^{31}P\{^{1}H\}$ NMR (δ, in $CDCl_3$): 30.4 ($^{1}J_{PW}=166.4$ Hz, $^{2}J_{PW}=81.4$ Hz)

3.3. Synthesis of $(OC)_5Mo(\mu$-*trans*-**1**$)Mo(CO)_5$ (**2b**)

2b was prepared as described above for **2a**, using $Mo(CO)_6$. ^{1}H NMR (δ, in $CDCl_3$): 7.20–7.42 (m, 10H, Ph), 7.83 (t, $J_{HH}=7.1$ Hz, $J_{PH}=8.1$ Hz, 2H, 2,7-naph), 8.03 (m, 2H, 3,5-naph), 8.16 (d, $J_{HH}=8.3$ Hz, 2H, 4,5-naph). $^{13}C\{^{1}H\}$ NMR (δ, in $CDCl_3$): 128.1 (t, $J_{PC}=4.9$ Hz), 129.0 (t, $J_{PC}=4.0$ Hz), 130.4 (s), 131.3 (s), 133.0 (t, $J_{PC}=4.3$ Hz), 133.3 (t, $J_{PC}=7.3$ Hz), 133.4 (t, $J_{PC}=8.7$ Hz), 135.5 (t, $J_{PC}=15.0$ Hz), 137.2 (t, $J_{PC}=11.6$ Hz), 138.8 (t, $J_{PC}=4.3$ Hz), 204.4 (t, $J_{PC}=4.0$ Hz, *cis*-CO), 209.0 (t, $J_{PC}=13.8$ Hz, *trans*-CO). $^{31}P\{^{1}H\}$ NMR (δ, in $CDCl_3$): 49.1.

3.4. Synthesis of $(OC)_5Cr(\mu$-*trans*-**1**$)Cr(CO)_5$ (**2c**)

2c was prepared as described above for **2a**, using $Cr(CO)_6$. ^{1}H NMR (δ, in $CDCl_3$): 7.35–7.47 (m, 10H, Ph), 7.83 (t, $J_{HH}=7.1$ Hz, $J_{PH}=8.2$ Hz, 2H, 2,7-naph), 8.04 (m, 2H, 3,5-naph), 8.15 (d, $J_{HH}=8.3$ Hz, 2H, 4,5-naph). $^{13}C\{^{1}H\}$ NMR (δ, in $CDCl_3$): 128.0 (t, $J_{PC}=4.9$ Hz), 129.2 (t, $J_{PC}=4.0$ Hz), 130.5 (s), 131.4 (s), 132.9 (t, $J_{PC}=6.1$ Hz), 133.0 (t, $J_{PC}=4.9$ Hz), 133.3 (t, $J_{PC}=7.3$ Hz), 134.5 (t, $J_{PC}=15.0$ Hz), 136.6 (t, $J_{PC}=12.0$ Hz), 137.9 (t, $J_{PC}=5.5$ Hz), 215.1 (t, $J_{PC}=5.5$ Hz, *cis*-CO), 220.5 (t, $J_{PC}=2.5$ Hz, *trans*-CO). $^{31}P\{^{1}H\}$ NMR (δ, in $CDCl_3$): 71.7.

3.5. Synthesis of $W($*trans*-**1**$)(CO)_5$ (**3a**)

$W(CO)_6$ (970 mg, 2.8 mmol) dissolved in THF was irradiated by a mercury lamp for 2.5 h. To a $W(CO)_5$(thf) solution thus obtained was added *trans*-**1** (660 mg, 1.9 mmol) dissolved in a minimum amount of THF. The solution was stirred for 4 h, and THF was removed in vacuo. The residue was dissolved in $CHCl_3$ and passed through a short silica gel column (2 cm ID×2 cm). The product **3a** was separated from **2a** and unreacted $W(CO)_6$ by the preparative scale GPC column. Yield: 842 mg (66%). IR (ν_{CO}, cm^{-1}, in THF): 2072, 1940. ^{1}H NMR (δ, in $CDCl_3$): 7.10 (m, 2H, Ph), 7.15–7.40 (m, 8H, Ph), 7.59 (m, $J_{HH}=7.2$ Hz, $J_{HH}=8.1$ Hz, $J_{PH}=2.4$ Hz, 1H, 6-naph), 7.76 (m, $J_{HH}=7.2$ Hz, $J_{HP}=7.2$ Hz, $J_{PH}=0.9$ Hz, 1H, 7-naph), 7.89 (m, $J_{HH}=7.0$ Hz, $J_{HH}=8.1$ Hz, $J_{PH}=2.9$ Hz, 1H, 3-naph), 7.99 (d, $J_{HH}=8.3$ Hz, 1H, 5-naph), 8.13 (bd, $J_{HH}=8.2$ Hz, 1H, 4-naph), 8.30 (m, $J_{HH}=7.7$ Hz, $J_{PH}=0.8$ Hz, 1H, 7-naph). $^{13}C\{^{1}H\}$ NMR (δ, in $CDCl_3$): 127.3 (d,

$J_{PC}=9.3$ Hz), 128.0 (d, $J_{PC}=8.7$ Hz), 128.4 (d, $J_{PC}=9.3$ Hz), 128.8 (s), 129.0 (dd, $J_{PC}=1.9$ Hz, $J_{PC}=8.1$ Hz), 129.3 (s), 130.1 (dd, $J_{PC}=8.1$ Hz, $J_{PC}=10.0$ Hz), 130.6 (d, $J_{PC}=1.3$ Hz), 130.7 (d, $J_{PC}=1.9$ Hz), 132.4 (dd, $J_{PC}=4.4$ Hz, $J_{PC}=26.1$ Hz), 133.3 (d, $J_{PC}=6.2$ Hz), 133.9 (dd, $J_{PC}=1.2$ Hz, $J_{PC}=11.2$ Hz), 134.6 (d, $J_{PC}=23.6$ Hz), 134.9 (d, $J_{PC}=5.6$ Hz), 135.2 (d, $J_{PC}=5.5$ Hz), 138.0 (dd, $J_{PC}=2.5$ Hz, $J_{PC}=22.4$ Hz), 138.4 (dd, $J_{PC}=17.4$ Hz, $J_{PC}=32.9$ Hz), 139.6 (d, $J_{PC}=23.0$ Hz), 140.4 (dd, $J_{PC}=1.9$ Hz, $J_{PC}=8.7$ Hz), 196.0 (d, $J_{PC}=6.9$ Hz, $J_{CW}=125.3$ Hz), 198.5 (d, $J_{PC}=24.2$ Hz). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): −8.8 ($J_{PP}=219.9$ Hz), 13.1 ($J_{PP}=219.9$ Hz, $J_{PW}=235.7$ Hz).

3.6. Synthesis of Mo(trans-**1**)(CO)$_5$ (**3b**)

3b was prepared as described above for **3a**, using Mo(CO)$_6$. IR (ν_{CO}, cm^{-1}, in THF): 2073, 1949. ^1H NMR (δ, in $CDCl_3$): 7.08 (m, 2H, Ph), 7.18–7.37 (m, 8H, Ph), 7.59 (m, $J_{HH}=7.3$ Hz, $J_{HH}=8.1$ Hz, $J_{PH}=2.6$ Hz, 1H, 6-naph), 7.75 (t, $J_{HH}=7.2$ Hz, $J_{HP}=7.2$ Hz, 1H, 7-naph), 7.87 (m, $J_{HH}=7.1$ Hz, $J_{HH}=7.9$ Hz, $J_{PH}=2.7$ Hz, 1H, 3-naph), 7.98 (d, $J_{HH}=8.3$ Hz, 1H, 5-naph), 8.13 (d, $J_{HH}=8.1$ Hz, 1H, 4-naph), 8.30 (m, $J_{HH}=7.1$ Hz, $J_{PH}=9.5$ Hz, 1H, 2-naph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 127.3 (d, $J_{PC}=9.4$ Hz), 128.0 (d, $J_{PC}=8.7$ Hz), 128.4 (d, $J_{PC}=8.7$ Hz), 128.7 (s), 128.9 (dd, $J_{PC}=1.2$ Hz, $J_{PC}=8.1$ Hz), 129.0 (s), 130.1 (dd, $J_{PC}=8.1$ Hz, $J_{PC}=10.6$ Hz), 130.4 (d, $J_{PC}=1.3$ Hz), 130.6 (d, $J_{PC}=1.9$ Hz), 132.3 (dd, $J_{PC}=3.7$ Hz, $J_{PC}=26.1$ Hz), 133.3 (d, $J_{PC}=6.2$ Hz), 133.7 (d, $J_{PC}=12.4$ Hz), 134.8 (d, $J_{PC}=23.0$ Hz), 134.9 (d, $J_{PC}=5.0$ Hz, $J_{PC}=22.3$ Hz), 138.2 (dd, $J_{PC}=3.1$ Hz, $J_{PC}=17.8$ Hz), 138.6 (dd, $J_{PC}=16.8$ Hz, $J_{PC}=27.4$ Hz), 139.7 (d, $J_{PC}=23.6$ Hz), 140.5 (dd, $J_{PC}=1.8$ Hz, $J_{PC}=7.4$ Hz), 204.7 (d, $J_{PC}=9.3$ Hz, *cis*-CO), 209.6 (d, $J_{PC}=24.8$ Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): −8.5 ($J_{PP}=220$ Hz), 33.7 ($J_{PP}=220$ Hz).

3.7. Synthesis of Cr(trans-**1**)(CO)$_5$ (**3c**)

3c was prepared as described above for **3a**, using Cr(CO)$_6$. IR (ν_{CO}, cm^{-1}, in THF): 2065, 1987(sh). ^1H NMR (δ, in $CDCl_3$): 7.15–7.35 (m, 10H, Ph), 7.50 (m, $J_{HH}=7.3$ Hz, $J_{HH}=8.4$ Hz, $J_{PH}=2.6$ Hz, 1H, 6-naph), 7.68 (t, $J_{HH}=7.3$ Hz, $J_{HP}=7.3$ Hz, 1H, 7-naph), 7.83 (m, $J_{HH}=7.1$ Hz, $J_{HH}=8.4$ Hz, $J_{PH}=2.9$ Hz, 1H, 3-naph), 7.91 (d, $J_{HH}=8.1$ Hz, 1H, 5-naph), 8.08 (d, $J_{HH}=8.3$ Hz, 1H, 4-naph), 8.39 (m, $J_{HH}=7.1$ Hz, $J_{HH}=0.7$ Hz, $J_{PH}=9.0$ Hz, 1H, 2-naph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 127.3 (d, $J_{PC}=9.4$ Hz), 127.9 (d, $J_{PC}=8.7$ Hz), 128.4 (d, $J_{PC}=9.4$ Hz), 128.7 (s), 128.9 (dd, $J_{PC}=1.9$ Hz, $J_{PC}=8.1$ Hz), 129.0 (br), 130.0 (d, $J_{PC}=9.3$ Hz), 130.2 (d, $J_{PC}=8.7$ Hz), 130.6 (d, $J_{PC}=1.9$ Hz), 130.7 (d, $J_{PC}=1.9$ Hz), 132.1 (dd, $J_{PC}=3.7$ Hz, $J_{PC}=26.1$ Hz), 133.2 (d, $J_{PC}=6.2$ Hz), 133.5 (dd, $J_{PC}=1.3$ Hz, $J_{PC}=10.6$ Hz), 133.9 (d, $J_{PC}=22.9$ Hz), 135.2 (d, $J_{PC}=5.6$ Hz, $J_{PC}=22.9$ Hz), 138.0 (d, $J_{PC}=16.8$ Hz, $J_{PC}=3.7$ Hz), 138.2 (dd, $J_{PC}=18.0$ Hz, $J_{PC}=28.0$ Hz), 139.6 (d, $J_{PC}=23.0$ Hz), 140.4 (dd, $J_{PC}=1.8$ Hz, $J_{PC}=8.0$ Hz), 215.6 (d, $J_{PC}=12.4$ Hz, *cis*-CO), 221.0 (d, $J_{PC}=5.6$ Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): −8.1 ($J_{PP}=228$ Hz), 52.0 ($J_{PP}=227$ Hz).

3.8. Conversion of trans-**3** to cis-**3**

Tungsten complex *trans*-**3a**, molybdenum complex *trans*-**3b**, and chromium complex *trans*-**3c** were each dissolved in toluene and sealed in NMR tubes, which were dipped in an oil bath at 100 °C and $^{31}P\{^1H\}$ NMR spectra were recorded at appropriate intervals. Since *cis*-**3a**–**c** formed were not isolated successfully, only $^{31}P\{^1H\}$ NMR data were given here. The tungsten complex: $^{31}P\{^1H\}$ NMR (δ, in toluene): −1.7 ($J_{PP}=238$ Hz, $J_{PW}=226$ Hz), 2.7 ($J_{PP}=236$ Hz). The molybdenum complex: $^{31}P\{^1H\}$ NMR (δ, in toluene): −6.6 ($J_{PP}=243$ Hz), 23.2 ($J_{PP}=243$ Hz). The chromium complex: $^{31}P\{^1H\}$ NMR (δ, in toluene): −9.1 ($J_{PP}=252$ Hz), 47.3 ($J_{PP}=252$ Hz).

3.9. Synthesis of (OC)$_5$W(μ-cis-**1**)W(CO)$_5$ (cis-**2a**)

Trans-**3a** (235 mg, 0.35 mmol) was dissolved in toluene and heated at 100 °C for 24 h. To a mixture of the *cis* and *trans* isomers was added W(CO)$_5$(thf) generated from W(CO)$_6$ (177 mg, 0.5 mmol). After stirring overnight, the solvents were removed in vacuo. The residue was passed through a short silica gel column. The effluent was a 1:3 mixture of *cis*–*trans*-**2a**. Complete separation of the *cis* isomer from the *trans* was attained by a recycling HPLC with the preparative scale GPC column (over 30 times of recycling). ^1H NMR (δ, in $CDCl_3$): 6.57 (m, 4H, m-Ph), 6.93 (t, $J_{HH}=7.8$, $J_{PH}=7.8$, 4H, o-Ph), 7.14 (2H p-Ph), 7.84 (m, 2H, 2,7-naph), 7.98 (m, 2H, 3,5-naph), 8.13 (d, $J_{HH}=8.2$ Hz, 2H, 4,5-naph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 127.9 (t, $J_{PC}=4.9$ Hz), 128.2 (t, $J_{PC}=4.0$ Hz), 130.1 (s), 130.9 (s), 131.6 (t, $J_{PC}=7.2$ Hz), 133.2 (t, $J_{PC}=6.5$ Hz), 133.6 (t, $J_{PC}=10.9$ Hz), 134.8 (t, $J_{PC}=16.7$ Hz), 136.9 (s), 196.6 (t, $J_{PC}=2.5$ Hz, $J_{CW}=126$ Hz, *cis*-CO), 197.7 (t, $J_{PC}=14.0$ Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 29.3 ($J_{PW}=163$ Hz, $J_{PW}=94$ Hz).

3.10. Synthesis of (OC)$_5$Mo(μ-cis-**1**)Mo(CO)$_5$ (cis-**2b**) and (OC)$_5$Cr(μ-cis-**1**)Cr(CO)$_5$ (cis-**2c**)

cis-**2b** and *cis*-**2c** were prepared as described above for *cis*-**2a**. Since complete separation of the *cis* isomer from the *trans* was not successful, only $^{31}P\{^1H\}$ NMR spectra were recorded. *cis*-**2b**: $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 46.5. *cis*-**2c**: $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 68.0.

Table 1
Crystallographic data

	Trans-**1**	*Trans*-**2a**	*Trans*-**3a**	*Cis*-**2a**
Formula	$C_{22}H_{16}P_2$	$C_{36}H_{24}O_{11}P_2W_2$	$C_{27}H_{16}O_5P_2W$	$C_{32}H_{16}O_{10}P_2W_2$
Crystal color	Colorless	Yellow	Yellow	Yellow
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	$C2/c$ (#15)	$P2_1/a$ (#14)
a (Å)	7.8660(1)	10.5220(1)	26.7690(3)	12.2040(1)
b (Å)	14.6310(3)	17.2730(2)	10.7820(1)	14.4120(2)
c (Å)	15.7980(4)	20.3480(2)	17.6970(3)	18.7280(2)
α (°)	101.904(1)			
β (°)	93.904(1)	102.173(1)	106.739(1)	73.561(1)
γ (°)	101.495(2)			
V (Å^3)	1732.03(6)	3615.03(7)	4891.3(1)	3159.31(6)
Z	4	4	8	4
μ(Mo Kα) (cm^{-1})	2.50	65.14	48.96	74.43
Radiation (Å)	Mo Kα	Mo Kα	Mo Kα	Mo Kα
	0.71069	0.71069	0.71069	0.71069
No. of reflections				
Measured	7679	8438	5733	7774
Observed ($I > 3.00\ \sigma$ (I), $2\theta < 55°$)	6734	7520	4914	7040
No. variables	562	461	381	416
Reflection/parameter	11.98	16.31	12.90	16.92
p-factor	0.1530	0.0950	0.1070	0.1620
Residuals[a] R[b]; R_w[c]	0.039; 0.080	0.028; 0.052	0.024; 0.058	0.036; 0.086

[a] Function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o)] = [\sigma_c^2(F_o) + p^2F_o^2/4]^{-1}$, $\sigma_c(F_o)$=e.s.d. based on counting statistics and p is the p-factor.

[b] $R = \sum || F_o | - | F_c || / \sum | F_o |$.

[c] $R_w = [(\sum w(| F_o | - | F_c |)_2 / \sum wF_o^2)]^{1/2}$.

3.11. Crystallographic study

Suitable crystals of *trans*-**1**, *trans*-**2a**, *cis*-**2a**, and *trans*-**3a** were mounted on glass fibers. Crystallographic data are given in Table 1. All measurements were made on a Mac Science DIP2030 imaging plate area detector. The data were collected to a maximum 2θ value of 55.8° at −73 °C. Cell parameters and intensities for the reflection were estimated using the program packages of MacDENZO [15]. The structure was solved by direct methods and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using a teXsan crystallographic software package from the Molecular Structure Corporation [16].

4. Supplementary material

Crystallographic Information has been deposited with Cambridge Crystallographic Data Center, CCDC Nos. 234352 for **1**, 234353 for *trans*-**2a**, 234354 for **3a**, and 234355 for *cis*-**2a**. The data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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