Organometallics **1996,** *15,* 2399−2403

Optically Active Bimetallic Complexes with a Tantalum Atom as a Chiral Center. Synthesis, Characterization, and X-ray Structures of Two Diastereoisomers: $Cp'CpTa^*(CO)(\mu\text{-}PMe_2)W(CO)_4L^*$ ($Cp' = 1\text{-}^tBu\text{-}3,4\text{-}Me_2\text{-}C_5H_2$; $L^* =$ (*R*)-(+)-Phenyl(*o*-anisyl)methylphosphine (PAMP))

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Received January 25, 1996[⊗]

Reaction of the racemic metallophosphine $Cp'CpTa(CO)(PMe_2)$ (**1**; $Cp' = 1\text{-}^tBu\text{-}3,4\text{-}Me_2\text{-}C_5H_2$) with the tungsten fragment $[W(CO)_5]$ affords the corresponding μ-bimetallic phosphido complex **2**, which in a photochemical transformation gives the dibridged derivative $Cp'CpTa(\mu\text{-}CO)(\mu\text{-}PMe_2)W(CO)_4$ (**3**). Addition of an optically active phosphine (PAMP) to **3** leads to a pair of optically active diastereoisomers (**4a** and **4b**) which can be separated by fractionnal crystallization. Both diastereoisomers **4a** and **4b** crystallize in the orthorhombic noncentrosymmetric space group $P2_12_12_1$. X-ray structure determinations of **4a** and **4b** allowed the assignment of absolute configurations of the tantalum chiral centers (*S* for **4a** and *R* for **4b**). The absolute configuration of the phosphorus atom of the PAMP ligand is the same (*S*) in both structures.

Introduction

Organometallic stereochemistry has undergone intense development over the last few decades for two main reasons: chiral organometallic complexes may be employed from a mechanistic point of view for studying the effects of ligand substitutions or of reactions on the metal−ligand bond,[1] but catalytic or stoichiometric enantioselective organic syntheses are by far the major applications.[2] Chirality may arise from the presence of an asymmetric ligand or derive from the metal center, which lies in an asymmetric environment. As reviewed by Brunner[3] and Sokolov,[4] this latter structural possibility is frequently encountered in square-pyramidal and pseudotetrahedral complexes. The molecular structures of group 4, 5, and 6 metal bis(cyclopentadienyl) derivatives contain the metal atom in a pseudotetrahedral arrangement; the asymmetry of the metallic center thereby requires the presence of two different cyclopentadienyl rings. This feature can be readily achieved by introduction of alkyl substituents on one of the two Cp rings. We have already used such a strategy to synthesize and to resolve chiral bis(cyclopentadienyl)titanium derivatives.[5] For some time we have been interested in the building of bi- and triheterometallic systems based on metallophosphines as starting materials. These are the group 5 bis(cyclopentadienyl) derivatives.[6] To the best of our knowledge, no example of an optically active group 5 organometallic complex has been reported to date. We have therefore undertaken the synthesis of chiral metalloligands with the aim of their resolution and of the preparation of optically active polymetallic structures. We wish to report here our results in this stereochemical area.

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[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1996.

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S0276-7333(96)00049-0 CCC: $12.00

Experimental Section

General Materials and Measurements. All reactions were carried out under an argon atmosphere with use of standard Schlenk techniques. The solvents and eluants were dried and distilled under argon from sodium and benzophenone immediately before use. Column chromatography was performed under argon and with silica gel (70−230 mesh). Cp′CpTa(CO)(PMe$_2$) (**1**) and the optically active phosphine "(*R*)-PAMP" were prepared by previously reported procedures.[7,8]

^{1}H and ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer; chemical shifts are given in ppm relative to Me$_4$Si (^{1}H) or (external) H$_3$PO$_4$ (^{31}P). Infrared spectra were recorded on a Nicolet 205 IR-FT. CD spectra were recorded (at 25 °C) on a Jobin Yvon CD6 dichrograph, with THF solutions (1.0×10^{-3} M for **4a**, 6.6×10^{-4} M for **4b**, and 1.6×10^{-3} M for Cp$_2$Ta(CO)(μ-PMe$_2$)W(CO)$_4$PAMP[6h]) in a 1 cm cell. Elemental analyses (C, H) were performed by the "Service Central d'Analyse du CNRS" (Gif-sur-Yvette, France).

Synthesis of Cp′CpTa(CO)(μ-PMe$_2$)W(CO)$_5$ (2). To a solution of **1** (250 mg, 0.52 mmol) in 15 mL of THF was added an excess of W(CO)$_5$(THF) produced by irradiation of W(CO)$_6$ (210 mg, 0.60 mmol) in THF. Then, the mixture was stirred for 45 min at room temperature. The solvent was removed *in vacuo* and the crude reaction product chromatographed on silica gel with toluene as eluant. Recrystallization from THF/pentane (1:6) afforded 290 mg of green crystals of **2** (69%). IR (ν(CO), THF): 2051 (m), 1975 (s), 1913 (vs) cm^{-1}. Anal. Calcd for C$_{24}$H$_{28}$O$_6$PTaW: C, 35.67; H, 3.49. Found: C, 35.55; H, 3.47.

Synthesis of Cp′CpTa(μ-CO)(μ-PMe$_2$)W(CO)$_4$ (3). A solution of **2** (260 mg, 0.32 mmol) in 100 mL of THF was irradiated in Pyrex filtering vessels with a high-pressure Hanau TQ 150 mercury lamp for 6 h. After evaporation of the solvent, the crude product was chromatographed on silica gel. Elution with toluene/THF (4:1) afforded two fractions. The first band was unreacted **2** (50 mg). The second band was red. After the solvent was removed, **3** was obtained as a red solid. Yield: 130 mg (52%). IR (ν(CO), THF): 1999 (m), 1930 (s), 1908 (m), 1880 (s), 1705 (w) cm^{-1}.

Synthesis of Cp′CpTa(CO)(μ-PMe$_2$)W(CO)$_4$PMePh(*o*-An) (4). To a solution of **3** (130 mg, 0.17 mmol) in 40 mL of THF was added PAMP (40 mg, 0.17 mmol). After 30 min at room temperature, the solution changed from red to green. The solvent was then removed under reduced pressure, and the crude reaction product was chromatographed on silica gel with ether/pentane (6:14) as eluant. After the solvent was removed, a green solid was obtained. Yield: 160 mg (92%). IR (ν(CO), THF): 1993 (m), 1904 (m), 1885 (vs), 1867 (vs), 1839 (s) cm^{-1}. Anal. Calcd for C$_{37}$H$_{43}$O$_6$P$_2$TaW: C, 43.98; H, 4.29. Found: C, 43.31; H, 4.27.

Separation of the Diastereoisomers 4a and 4b. **4** was dissolved in diethyl ether. The solution was concentrated close to saturation. Pentane was added, and the green solution was cooled to 5 °C for 2 days. Two types of crystals differing in shape and color (green needles for **4a** and brown pyramids for **4b**) were concurrently grown. Separation of crystals was carried out manually in order to perform crystallographic, NMR, and chiroptical studies. **4a:** optical rotation, $[\alpha]^{20}_{578}$ +66°, $[\alpha]^{20}_{546}$ +117°, $[\alpha]^{20}_{436}$ +301° (*c* 1, THF). **4b:** optical rotation, $[\alpha]^{20}_{578}$ −82°, $[\alpha]^{20}_{546}$ −128°, $[\alpha]^{20}_{436}$ −434° (*c* 0.66, THF).

X-ray Structure Determination. The sizes of the crystals used for data collections carried out on an Enraf-Nonius CAD4 diffractometer and the pertinent crystallographic data are given in Table 1. The unit cells were determinated from 25 reflections selected by the CAD4 automatic routines. All calculations were carried out by use of the MOLEN package[9] with neutral-atom scattering factors.[10] Intensities were corrected for Lorentz and polarization effects as well as for linear decay.

Table 1. Crystallographic Data for Cp′CpTa(CO)(μ-PMe$_2$)W(CO)$_4$PAMP (4a,b)

	4a	4b
mol formula	WTaP$_2$O$_6$C$_{37}$H$_{43}$	WTaP$_2$O$_6$C$_{37}$H$_{43}$
fw	1010.5	1010.5
cryst size, mm	0.3 × 0.15 × 0.15	0.4 × 0.3 × 0.3
cryst syst	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
cell dimens		
a, Å	13.965(5)	10.122(2)
b, Å	18.203(4)	11.395(3)
c, Å	14.604(6)	32.734(6)
V, Å^3	3712(2)	3775(1)
Z	4	4
d_{calcd}, g cm^{-3}	1.808	1.778
F(000)	1960	1960
linear abs, μ, cm^{-1}	62.015	60.975
radiation, Å	λ(Mo Kα) = 0.710 73	λ(Mo Kα) = 0.710 73
θ range, deg	2−25	2−25
scan type	ω−2θ	ω
scan speed, deg min^{-1}	1.7−8.3	1.5−8.3
scan width, deg	$\Delta\omega = 0.47 + 0.347 \tan\theta$	$\Delta\omega = 0.90 + 0.347 \tan\theta$
no. of rflns measd	8212	8024
temp, K	296(1)	296(1)
decay, %	−4.7, corrected	−21, corrected
cutoff for obsd data	$I \geq 3\sigma(I)$	$I \geq 3\sigma(I)$
no. of unique obsd data (NO)	5218	5513
no. of variables (NV)	535	364
R(*F*)	0.038	0.064
$R_w(F)$	0.044	0.078
wt, $w^{-1} = [\sigma^2(I) + (pF_o{}^2)^2]^{1/2}$, *p*	0.040	0.060
GOF	0.405	1.349
$\rho_{\max}/\rho_{\min}$, e Å^{-3}	1.12^a/−0.34	1.80^a/−0.52

^{a} Close to the tantalum atom.

Systematic extinctions indicated the same noncentrosymmetric orthorhombic space group, $P2_12_12_1$, for both crystals. The structures were solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. All nonhydrogen atoms in **4a** were refined with anisotropic thermal parameters. Because of the poor quality of the crystals of **4b**, some non-hydrogen atoms were treated in an isotropic model. The correct initial choice of enantiomorph for **4a** and **4b** was checked by inversion of all positional parameters. In both cases, an increase of *R* factors (from 0.040 to 0.051 for **4a** and from 0.068 to 0.075 for **4b**) was observed without improvement of estimated standard deviations. The hydrogen atoms were placed in calculated positions and included in the final cycles of refinements in a riding model with B_{iso} fixed at 1.3B_{eq} for the carbon atoms bearing them. The atomic coordinates for the structures of **4a** and **4b** are given in Tables 2 and 3, respectively (Supporting Information).

Results and Discussion

The racemic metallophosphine [Cp′CpTa(CO)PMe$_2$] (**1**; Cp′ = 1-^{t}Bu-3,4-Me$_2$-C$_5$H$_2$) is obtained as a green solid according to the procedure outlined in Scheme 1 by reaction of the chiral carbonyl hydride Cp′CpTa(CO)(H)[7] with PMe$_2$Cl followed by treatment with KOH.

Stereostability at the asymmetric tantalum center in **1** is clearly evidenced by the ^{1}H NMR spectrum, which

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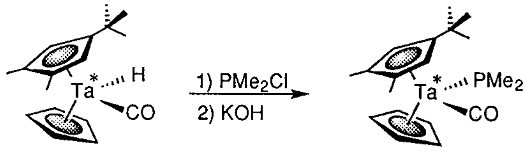
Table 4. ^{1}H and ^{31}P NMR Data for 1−3

complex	^{1}H NMR (ppm, C_6D_6)		^{31}P NMR (ppm, C_6D_6)
	Cp and Cp′	PMe$_2$	
1	4.46 (s, 5H)	1.50 (s, br, 6H)	−91.5
	4.39 (dd, 7^a and 2.5 Hz, 1H)		
	3.82 (d, 2.5 Hz, 1H)		
	2.03 (s, 3H, *Me*)		
	1.94 (s, 3H, *Me*)		
	0.97 (s, 9H, ^{t}*Bu*)		
2	4.52 (d, 1.9 Hz,^{a} 5H)	2.00 (d, 5.1 Hz, 3H)	−118.8 (s, J_{PW} = 171 Hz)
	3.84 (s, br, 1H)	1.66 (d, 5.6 Hz, 3H)	
	3.69 (s, br, 1H)		
	1.85 (s, 3H, *Me*)		
	1.45 (s, 3H, *Me*)		
	1.00 (s, 9H, ^{t}*Bu*)		
3	4.49 (d, 2.2 Hz,^{a} 5H)	1.92 (d, 8.5 Hz, 3H)	34.4 (s, J_{PW} = 163 Hz)
	3.92 (d, 2.7 Hz, 1H)	1.46 (d, 8.5 Hz, 3H)	
	3.83 (dd, 5.6^a and 2.7 Hz, 1H)		
	1.66 (s, 3H, *Me*)		
	1.52 (s, 3H, *Me*)		
	0.89 (s, 9H, ^{t}*Bu*)		

^{a} ^{31}P coupling.

Scheme 1

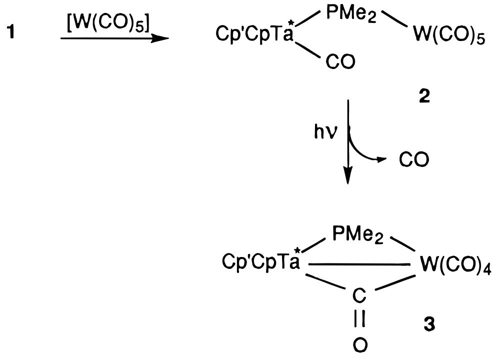


1

displays two sets of two different signals for the two methyl groups and the two ring protons of the substituted cyclopentadienyl ligand. Furthermore, a temperature dependence is observed for the resonance signal of the PMe$_2$ group. As mentioned in Table 4 this signal appears as a broad singlet at 295 K and as a doublet ($^2J_{PH}$ = 4 Hz) at 330 K, whereas two well-resolved doublets ($\Delta\nu$ = 56 Hz, $^2J_{PH}$ = 4 Hz) are displayed when the temperature is decreased to 260 K. This behavior is indicative of a low stereostability at the phosphorus center, as has been previously reported for related niobo derivatives.[6d] According to our previous results dealing with the reactivity of the unsubstituted metallophosphine [Cp$_2$Ta(CO)(PMe$_2$)] toward group 6 pentacarbonyl fragments,[6h] complex **1** is allowed to react with the tungsten fragment [W(CO)$_5$] in order to obtain the corresponding bimetallic derivative **2**. A photochemical treatment of **2** leads to the μ-PMe$_2$, μ-CO dibridged complex **3** in a moderate yield (52%).

NMR data (Table 4) support the structures ascribed to **2** and **3**, and the corresponding patterns are similar to those observed for the complexes with nonsubstituted Cp rings described earlier.[6h] In particular, for complex **3** the μ-CO IR absorption centered at 1705 cm^{-1} indicates the presence of the bridging carbonyl group. The ^{31}P chemical shifts of the dimethylphosphido ligand merit some comments. The corresponding resonance in metallophosphine **1** is only slightly deshielded with respect to that reported for PMe$_2$H (−99 ppm).[11] The negative coordination chemical shift[12] is observed upon

Scheme 2



the complexation of this metallophosphine to the W(CO)$_5$ fragment. Such a behavior of the phosphorus nuclei is easily explained by the participation of the nonlocal diamagnetic contribution in the overall shielding.[13] In this context, the ^{31}P resonance in **3** (+34.4 ppm) is strongly deshielded and indicates the presence of a direct Ta−W bond.[14]

We have recently shown that Lewis bases L (isonitriles or phosphines) are able to cleave regiospecifically the metal−metal bond in dibridged structures of type **3**, Cp$_2$Ta(μ-CO)(μ-PMe$_2$)M(CO)$_4$. We have already shown that such a cleavage leads to the formation of an M(CO)$_4$L fragment bound to the metallocene through a phosphido bridge.[6h] The stereo- or electrochemical opening of the metal−metal bond or of the carbonyl bridge by the nucleophiles depends on the size of the incoming ligand L as well as on that of the metal M. *Trans* geometries are favored with a small chromium atom, but the *cis* ones may be easily formed in the presence of larger metals such as tungsten. The size of the L ligand also influences the nature of geometrical isomers: small phosphines give *cis* geometries, while the bulkier ones favor the *trans* isomers. In the case of tungsten, a *cis* arrangement is exclusively formed, except for the bulky PPh$_3$ phosphine, which gives a small amount of *trans* isomer (5%). Our strategy of resolution uses these observations.

The room-temperature reaction of **3** with the very bulky, optically active NMDPP (neomenthyldiphenylphosphine) is unsuccessful; heating causes significant degradation of the starting dibridged complex with regeneration of some amount of **2**. In contrast, reaction of **3** with PAMP ((*R*)-(+)-phenyl(*o*-anisyl)methylphosphine; ee = 98%) proceeds quickly, affording after workup the pair of diastereoisomers **4a** and **4b**.

4a and **4b** show well-separated signals in ^{1}H and ^{31}P NMR spectra (Table 5); no diastereoselectivity can be deduced from the *ratio* of their integrated intensities. Attempts to perform a separation of diasteroisomers by chromatography lead only to a slight enrichment in one form; however, crystallization of the mixture **4a** + **4b** from ether/pentane affords two kinds of distinctly colored crystals which can be easily manually separated.

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Table 5. ^{1}H and ^{31}P NMR Data for 4a and 4b

	^{1}H NMR (ppm, C_6D_6)			^{31}P NMR (ppm, C_6D_6)	
complex	Cp and Cp′	PMe_2	PMePh(*o*-An)	PMe_2	PMePh(*o*-An)
4a	4.69 (d, 2 Hz,[a] 5H) 3.85 (s, br, 1H) 3.80 (s, br, 1H) 2.14 (d, 1.7 Hz,[a] 3H, *Me*) 1.61 (s, 3H, *Me*) 1.04 (s, 9H, ^{t}*Bu*)	1.73 (d, 4.4 Hz, 3H) 1.47 (d, 5.1 Hz, 3H)	6.4−8 (m, *Ph*) 3.30 (s, O*Me*) 2.11 (d, 5.4 Hz, P*Me*)	−117.7 (d, 30 Hz)	−13.9 (d, 30 Hz)
4b	4.72 (d, 2 Hz,[a] 5H) 3.83 (s, br, 1H) 3.76 (s, br, 1H) 2.12 (d, 1.7 Hz,[a] 3H, *Me*) 1.60 (s, 3H, *Me*) 1.02 (s, 9H, ^{t}*Bu*)	1.69 (d, 4.4 Hz, 3H) 1.37 (d, 5.3 Hz, 3H)	6.4−8 (m, *Ph*) 3.25 (s, O*Me*) 2.15 (d, 5.3 Hz, P*Me*)	−118.1 (d, 30 Hz)	−15.4 (d, 30 Hz)

[a] ^{31}P coupling.

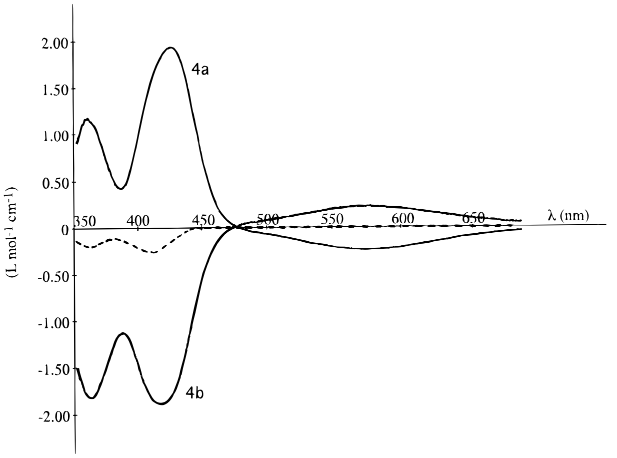
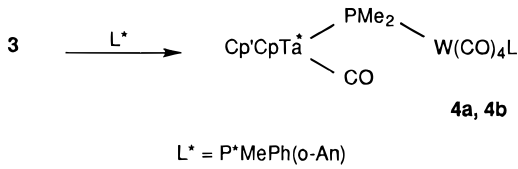


Figure 1. Circular dichroism curves of **4a** and **4b** (solid line) and $Cp_2Ta(CO)(\mu\text{-}PMe_2)W(CO)_4PAMP$ (dashed line).

Scheme 3



The purity of each sample has been checked by NMR spectroscopy.

It may be assumed that the stereochemistry of the chiral phosphine remains unchanged upon its coordination to the tungsten atom; therefore, the optical isomers **4a** and **4b**, which differ only in the absolute configuration at their tantalum centers, are expected to be optically active in solution. As mentioned in the literature,[3,5,15] it can be expected that these two diasteroisomers should display mirror-image CD spectra.

Figure 1 shows the CD curves obtained on THF solutions of **4a** and **4b** (solid line) and recorded in the 350−650 nm region. These CD spectra are defined by two intense Cotton effects, at about 360 and 420 nm, and by another weak signal of opposite sign at about 580 nm. As expected, they show an almost enantiomeric (mirror-image) shape, which must arise from the enantiomeric relationship between the tantalum centers in these two diastereoisomers. To confirm the domination of the tantalum chromophore, the CD spectrum obtained for a THF solution of $Cp_2Ta(CO)(\mu\text{-}PMe_2)W(CO)_4PAMP$ (dotted line) is reported in Figure 1. The very weak intensity of this curve clearly demonstrates the minor contribution of the $W(CO)_4PAMP$ moiety to the chiroptical properties of **4a** and **4b**.

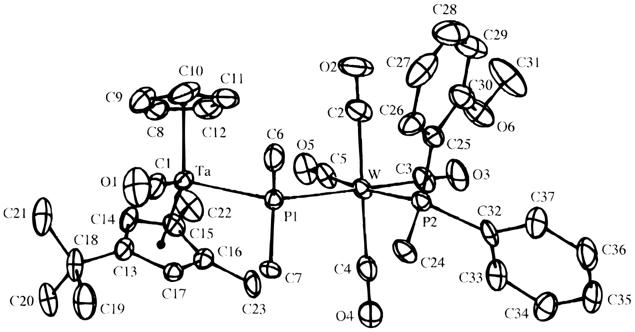


Figure 2. Molecular structure of **4a** (50% probability level).

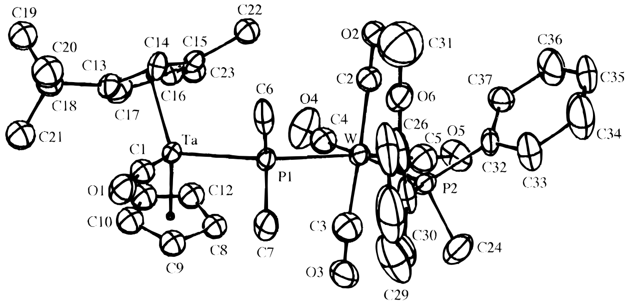


Figure 3. Molecular structure of **4b** (30% probability level).

The absolute configurations of the tantalum and of the phosphorus atoms have been clearly defined from the structure determination of **4a** and **4b**.

The crystal structures of **4a** and **4b** are built from discrete dinuclear molecules. These molecules contain the tantalocene (pseudotetrahedral geometry) and tetracarbonylphosphinotungsten (distorted octahedron) moieties singly bridged by the dimethylphosphide ligand. The overall geometries of both molecules are closely related and exhibit similar metric parameters (Table 6). They form a pair of diastereoisomers which differ from one another in the optical isomerism of the metallic (Ta) center. The chiralities of the asymmetric phosphorus atoms (P2) are the same and correspond to that of the free PAMP ligand.[8] Thus, the diastereoisomer **4a** is *S(Ta),S(P)*, while **4b** is *R(Ta),S(P)* if we assume the following priority numbers over the tantalum atom:[16] 1 (Cp′ ligand), 2 (Cp ligand), 3 (P atom), and 4 (carbonyl

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Table 6. Selected Bond Distances (Å) and Angles (deg) for Cp′CpTa(CO)(μ-PMe$_2$)W(CO)$_4$PAMP (4a,b)

	4a	**4b**
Ta−W	4.7723(7)	4.7598(9)
Ta−CP1	2.076	1.98
Ta−CP2	2.079	2.06
Ta−P1	2.685(3)	2.675(5)
Ta−C1	2.04(1)	1.99(2)
W−P1	2.628(3)	2.641(5)
W−P2	2.549(3)	2.511(6)
W−C2	2.02(2)	2.00(2)
W−C3	1.98(1)	1.95(3)
W−C4	2.02(1)	1.93(3)
W−C5	1.95(1)	2.04(3)
CP1−Ta−CP2	136.0	136.4
P1−Ta−C1	83.4(4)	82.4(7)
P1−W−P2	96.3(1)	99.8(2)
Ta−P1−W	127.8(1)	127.1(2)

C atom). The orientation of methyl substituents on the bridging phosphorus atom with respect to the metallocene Cp′CpTa-CO is of the *endo* type. The same *endo* structure has been already observed in the complexes Cp$_2$Nb(CO)(μ-PMe$_2$)W(CO)$_4$(PMe$_2$Ph)[17] and Cp$_2$Ta(CO)(μ-PMe$_2$S)W(CO)$_5$.[18] However, *exo*-type geometries are formed in the presence of bulkier substituents on the phosphorus atom such as Ph[19] and ^{i}Pr.[6d] Our previous extended Hückel calculations[6f,20] explain the influence of substituent size on the overall geometry of bimetallic complexes. In order to minimize the repulsions with the CO ligand, the methyl groups of the PMe$_2$ bridge in an *endo* conformation should be symmetrically displayed over the C1−Ta−P1 plane (as observed in both structures). Consequently, the tungsten atom should lie in this plane. However, the positions of the W atom deviate significantly from this plane: 0.46 Å in **4a** and 0.26 Å in **4b**. Thus, W(CO)$_4$L fragments are pushed toward the non-substituted and less hindered C$_5$H$_5$ ring. It is evident that steric intramolecular effects operate in the determination of the overall molecular geometry. It is worth noting that the conformations of the chiral phosphine atoms (P2) are different in the crystals of **4a** and **4b**. This is shown by the values of the dihedral angles P1−W−P2/W−P2−C24, which are equal to 34.3 and 65.4° for **4a** and **4b**, respectively. The Ta−P1 distances of 2.68 Å are long but correspond well with the values found for other group 5 metallocene−bridging phosphido ligands. The W−P1 distances of 2.628(3) Å (**4a**) and 2.641(5) Å (**4b**) are also long and together with the largely opened Ta−P1−W angles (127.85(1) and 127.1(2)°) indicate the presence of steric repulsions between both organometallic fragments. Thus, as previously stated, the metallophosphines Cp$_2$M(CO)PR$_2$ are very bulky ligands.[6,21] The W−P2 distances of 2.549(3) Å (**4a**) and 2.511(6) Å (**4b**) are short, as expected, and fall in the range observed for other *cis*-M(CO)$_4$ (M = Mo,W; 2.52−2.56 Å) complexes.[22] They are, however, shorter than those found in Fe(C$_5$Me$_4$PPh$_2$)$_2$W(CO)$_4$ (2.60 Å)[23] and in [Cp$_2$Mo(H)(μ-PMe$_2$)]$_2$W(CO)$_4$ (2.62 Å),[24] where the phosphorus atoms are of the “metallophosphine” type. The P1−W−P2 angles (96.3(1) and 99.8(2)°) fall in the range usually observed in *cis*-M(CO)$_4$ diphosphines (87−97°)[22] but are smaller than in Cp$_2$Zr(H)(μ-PPh$_2$)$_2$W(CO)$_4$ (103.3(1)°)[25] and in [Cp$_2$Mo(H)(μ-PMe$_2$)]$_2$W(CO)$_4$ (105.1(1)°).[24]

Supporting Information Available: For **4a** and **4b**, tables of X-ray crystallographic data, including atomic coordinates, anisotropic thermal parameters, and interatomic distances and angles and figures giving stereoviews (15 pages). Ordering information is given on any current masthead page.

OM9600497

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