

Phosphine Boranes in Coordination Chemistry: An Efficient Method for the Synthesis of Chiral and Achiral Organophosphorus Pentacarbonyltungsten Complexes

Nancy Brodie and Sylvain Jugé*

University of Cergy Pontoise, EA 1389, 5 Mail Gay Lussac, 95031 Cergy Pontoise Cedex, France

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Organophosphorus boranes **1–6** and amine pentacarbonyltungsten complexes **14–20** react under mild conditions, to afford by ligand exchange the corresponding $W(CO)_5(PR_3)$ **21–26** derivatives in 63–92% yields. The use of piperazine **13** as a diamine tungsten substituent permits a tandem reaction which removes the borane group and leads to the formation of the corresponding organophosphorus tungsten complex. The stereochemistry of the formation of pentacarbonyltungsten complexes from tertiary chiral organophosphorus borane compounds proceeds with a high stereoselectivity and retention of configuration at the chiral P center.

Introduction

In recent years, significant strides have been achieved in the asymmetric synthesis of phosphine ligands owing to the use of the protecting group borane (BH_3).^{1–5} The presence of BH_3

allows nucleophilic or electrophilic attack at the phosphorus center with recovery of the final compound under a nonracing decomplexation step.⁶ Moreover, borane adducts of phosphorus compounds are interesting in organophosphorus ligand synthesis because they possess an excellent reactivity and do not present any purification or storage problems. As part of our program concerning phosphine boranes in organophosphorus synthesis, the direct use of borane complexes in coordination chemistry was investigated.

Previously, we studied the asymmetric synthesis of organophosphorus compounds via an oxazaphospholidine complexed to a borane¹ or a pentacarbonyl tungsten.^{1b,7} The main purpose for this synthesis was the regio- and stereoselective ring opening of the complex via P–O bond cleavage. Unfortunately, it was not possible at the time to determine the stereochemistry of the tungsten products, although it had been well established for the analogous borane series.^{1d,e}

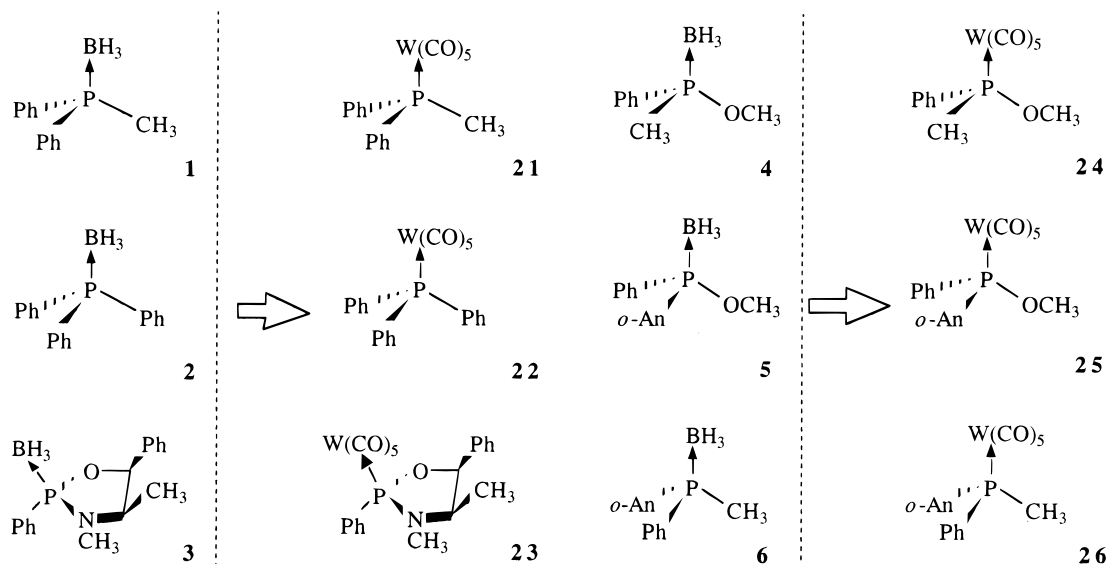
As the stereochemistry of bond formation or cleavage at the phosphorus center depends on the nucleophile substituents,³ it is important to know the absolute configuration of phosphorus compounds bearing sterically hindering groups such as $W(CO)_5$. On the other hand, new chiral tungsten complexes are of particular interest for use in applied organometallic chemistry.⁸ For these reasons, we report here the direct transformation of organophosphorus borane complexes **1–6** into chiral and achiral pentacarbonyltungsten derivatives **21–26** (Table 1).

Experimental Section

Solvents (THF, ether, toluene) were dried and freshly distilled over sodium/benzophenone under an argon atmosphere. Ethyl acetate and CH_2Cl_2 were of reagent grade and distilled before use. Flash chromatography was realized on silica gel (230–400 mesh; Merck).

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Table 1. Formation of the Pentacarbonyltungsten Complexes **21–26** by Ligand Exchange with the Organophosphorus Boranes **1–6**

All NMR spectral data were obtained on a Bruker DPX 250 (^1H , ^{13}C , ^{31}P) spectrometer with TMS as the internal reference for ^1H and ^{13}C NMR, and 85% phosphoric acid as the external reference for ^{31}P NMR. Infrared spectra were recorded on a Perkin-Elmer 1600 FT and a Bruker FT 45. Specific rotation values were determined at 20 °C on a Perkin-Elmer 241 polarimeter. Mass spectral analyses were performed on a Nermag R10-10C and a Kratos MS-50 for exact mass, at the laboratories of mass spectroscopy of ENSCP and University of P. & M. Curie (Paris), respectively. The major peak m/z is given with the intensity as the percent of the base peak in brackets. Elemental analyses were measured with a precision superior to 0.3%, at the Laboratories of Microanalyse of the University P. & M. Curie (Paris), and at the CNRS (Vernaison, France).

The diphenylmethyl phosphine borane **1** and triphenylphosphine borane **2** were prepared from the corresponding phosphine and borane dimethyl sulfide in THF and then recrystallized in hexane (**1**, mp = 55 °C; lit.^{6a} mp = 51 °C; **2**, mp = 189 °C; lit.⁹ mp = 189 °C). The complexes (2*S*,4*R*,5*S*)-(–)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidineborane **3**, (R)-(+)-[(O-methyl)methylphenylphosphinito]borane **4**, (S)-(+)-[(O-methyl) *o*-anisylphenylphosphinito]borane **5**, and (R)-(+)-*o*-anisylmethylphenylphosphineborane **6**, were prepared from the (+)-ephedrine according to the published procedure.^{1c,g}

The amine pentacarbonyltungsten complexes **14–20** were prepared from amines **7–13** and $\text{W}(\text{CO})_5(\text{THF})$, freshly prepared by irradiation of $\text{W}(\text{CO})_6$ in THF^{10,11} (Table 2). In the case of the pyrazine **12** and piperazine **13**, an excess of amine (5 equiv) was used to alleviate the formation of the bimetallic complex.

The pentacarbonyltungsten complexes of pyridine (py) **14**,¹¹ piperidine (pip) **15**,¹² benzo[*c*]cinnoline (bzc) **16**,¹³ and pyrazine (pyz) **17**¹⁴ were identified by their IR spectra as previously reported. The complexes of 4-phenylpyrimidine (4Ph-pm) **18**, pyrimidine (pm) **19**,^{14a}

and piperazine (pipz) **20** were characterized by ^1H NMR, IR, and elemental analyses.

4-Phenylpyrimidine Pentacarbonyltungsten Complex: $\text{W}(\text{CO})_5\cdot$ (4Ph-pm) **19.** Orange-yellow crystals; mp = 160–162 °C (3:7 hexane/ CH_2Cl_2); R_f = 0.3 (9:1 cyclohexane/AcOEt); IR (THF) $\bar{\nu}_{\text{CO}}$ cm^{-1} 2072 (w), 1974 (w), 1931 (s), 1902 (sh); ^1H NMR (CDCl_3) δ 9.47 (1H, s, H(2) pm), 8.98 (1H, d, $^3J_{\text{H}(6)\text{H}(5)}$ = 6 Hz, H(6) pm), 8.12 (2H, m, Ph), 7.71 (1H, d, $^3J_{\text{H}(5)\text{H}(6)}$ = 6 Hz, H(5) pm), 7.57 (3H, m, Ph); ^{13}C NMR (CDCl_3) δ 198.4 (CO(cis)), 163.3, 162.0, 132.7, 129.4, 127.4, 117.3; anal. calcd for $\text{C}_{15}\text{H}_9\text{N}_2\text{O}_5\text{W}$ (480), C, 37.50; H, 1.67; N, 5.83; found C, 37.83; H, 1.76; N, 5.90.

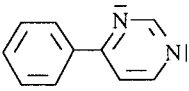
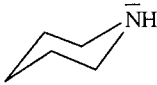
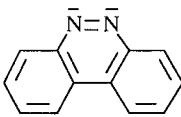
Pyrimidine Pentacarbonyltungsten Complex: $\text{W}(\text{CO})_5\cdot$ (pm) **19.**^{14a} Orange-yellow crystals; IR (THF) $\bar{\nu}_{\text{CO}}$ cm^{-1} 2071 (w), 1975 (w), 1932 (s), 1903 (sh); ^1H NMR (CDCl_3) δ 9.5 (1H, s, H(2)), 9.06 (1H, dd, $^3J_{\text{H}(6)\text{H}(5)}$ = 4.5 Hz, $^4J_{\text{H}(6)\text{H}(4)}$ = 2.2 Hz, H(6)), 8.84 (1H, dd, $^3J_{\text{H}(4)\text{H}(5)}$ = 4.9 Hz, $^4J_{\text{H}(4)\text{H}(6)}$ = 2.3 Hz, H(4)), 7.37 (1H, dd, $^3J_{\text{H}(5)\text{H}(4)}$ = 4.9 Hz, $^3J_{\text{H}(5)\text{H}(6)}$ = 2.3 Hz, H(5)); anal. calcd for $\text{C}_9\text{H}_4\text{N}_2\text{O}_5\text{W}$ (404), C, 26.73; H, 0.99; N, 6.93; found C, 26.91; H, 1.02; N, 7.09.

Piperazine Pentacarbonyltungsten Complex: $\text{W}(\text{CO})_5\cdot$ (pipz) **20.** Yellow crystals; mp = 141 °C (3:7 hexane/ CH_2Cl_2); R_f = 0.55 (8:2 cyclohexane/AcOEt); IR (THF) $\bar{\nu}_{\text{CO}}$ cm^{-1} 2068 (w), 1974 (m), 1922 (s), 1894 (sh); ^1H NMR (dioxane- d_8) δ 2.93 (2H, d, $^2J_{\text{H}_{\text{eq}}\text{H}_{\text{ax}}}$ = 12.6 Hz, $\text{H}_{\text{eq}}(1, 1')$), 2.76 (2H, qd, J = 11.3 Hz, $^3J_{\text{H}_{\text{ax}}\text{H}_{\text{eq}}}$ = 3.1 Hz, $\text{H}_{\text{ax}}(1, 1')$), 2.60 (2H, d, $^2J_{\text{H}_{\text{eq}}\text{H}_{\text{ax}}}$ = 12.6 Hz, $\text{H}_{\text{eq}}(2, 2')$), 2.46 (2H, qd, J = 11.2 Hz, $^3J_{\text{H}_{\text{eq}}\text{H}_{\text{ax}}}$ = 2.8 Hz, $\text{H}_{\text{ax}}(2, 2')$); ^{13}C NMR (dioxane- d_8) δ 60.1 (WNCCN), 49.1 (WNCCN); MS (EI) m/z (relative intensity) 395 (3), 382 (16), 354 (18), 326 (45), 324 (59), 322 (59), 296 (20), 268 (32), 238 (27), 211 (34), 85 (75), 56 (100); anal. calcd for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_5\text{W}$ (410), C, 26.34; H, 2.44; N, 6.83; found C, 26.30; H, 2.67; N, 7.16.

Procedure for Exchange Reactions. The exchange reactions were carried out in Schlenk tubes under an atmosphere of argon with stirring. Equivalent quantities of an amine pentacarbonyltungsten complex and a phosphine borane (1 mmol) were dissolved in dry THF (10 mL) and heated to the desired temperature (between 60 and 120 °C), and the progress of the reaction was monitored by IR spectroscopy. Formation of the phosphine pentacarbonyltungsten complex is indicated by a characteristic shift of the CO stretching frequency to higher energy in comparison to the amine adduct. After a 24 h period, the formation of $\text{W}(\text{CO})_6$ became predominant in most cases, so the exchange reactions were stopped. In contrast, only a very small amount of $\text{W}(\text{CO})_6$ was detected during the reactions with the piperazine complex **20**, even after several days. After solvent removal, the crude product was purified by flash chromatography using a mixture of cyclohexane/ethyl acetate as eluent to give the phosphine pentacarbonyltungsten complexes **21–26**. The pentacarbonyltungsten complexes $\text{W}(\text{CO})_5\text{PPh}_2\text{Me}$ **21**¹⁵

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Table 2. Amine Pentacarbonyltungsten Complexes **14–20** Used for Ligand Exchange

amine	W(CO) ₅ (amine)	amine	W(CO) ₅ (amine)
	W(CO) ₅ (py) 14		W(CO) ₅ (4Ph-pm) 18
	W(CO) ₅ (pip) 15		W(CO) ₅ (pm) 19
	W(CO) ₅ (bzc) 16		W(CO) ₅ (pipz) 20
	W(CO) ₅ (pyz) 17		

and W(CO)₅PPh₃ **22**^{15,16} were identified by their NMR and IR spectra as previously described.

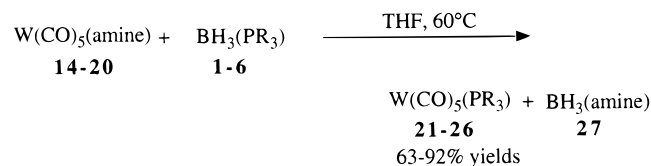
(2S,4R,5S)-(+)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine Pentacarbonyltungsten 23. Yellow solid; mp = 68 °C (hexane); TLC *R_f* = 0.4 (95:5 hexane/AcOEt); [α]_D = +32.1 (c 5, CHCl₃); IR (THF) $\bar{\nu}_{\text{CO}}$ cm⁻¹ 2075 (w), 1942 (br, s); ¹H NMR (CDCl₃) δ 7.56–7.31 (10H, m, arom), 5.41 (1H, dd, ³J_{H(4)H(5)}} = 6.6 Hz, ³J_{POCH} = 3 Hz, CHO), 3.36 (1H, m, ³J_{HH} = 6.4 Hz, CHN), 2.85 (3H, d, ³J_{PNCH} = 12.5 Hz, NCH₃), 0.75 (3H, d, ³J_{HH} = 6.5 Hz, CH₃); ¹³C NMR (CDCl₃) δ 196.0 (d, ²J_{PWCO} = 8.7 Hz, CO(cis)), 137.1, 130.5, 128.4 (d, *J*_{PC} = 13.3 Hz), 128.3, 127.9 (d, *J*_{PC} = 13 Hz), 126.9, 85.0 (d, ²J_{POC} = 8.8 Hz, CHO), 58.1 (CHN), 30.6 (d, ²J_{PNC} = 5 Hz, NCH₃), 14 (d, ³J_{PNCC} = 14 Hz, CH₃); ³¹P NMR (CDCl₃) δ +147.6 (m, ¹J_{PW} = 313 Hz); MS (EI) *m/z* (relative intensity) 597 (84), 595 (100), 565 (9), 511 (55), 455 (16); anal. calcd for C₂₁H₁₈NO₆PW (595), C, 42.29; H, 3.20; N, 2.46; found C, 42.35; H, 3.02; N, 2.35.

The minor epimer (2R,4R,5S) is detected in a 6:94 ratio, after the complexes **14** and **3** were heated in refluxing toluene for 24 h. ¹H NMR (CDCl₃) δ 5.60 (1H, d, ³J_{H(4)H(5)}} = 5.6 Hz, CHO), 3.77 (1H, m, ³J_{HH} = 6.3 Hz, CHN), 3.05 (3H, d, ³J_{PNCH} = 10.9 Hz, NCH₃), 0.46 (3H, d, ³J_{HH} = 6.7 Hz, CH₃).

(R)-(+)-[(O-Methyl)methylphenylphosphinite] Pentacarbonyltungsten 24. Uncrystallized; TLC *R_f* = 0.6 (9:1 hexane/AcOEt); [α]_D = +4.6 (c 1.1, CH₂Cl₂); IR (THF) $\bar{\nu}_{\text{CO}}$ cm⁻¹ 2080 (w), 1970 (br, vs); ¹H NMR (CDCl₃) δ 7.65 (m, 5H), 3.40 (3H, d, ³J_{POCH} = 10 Hz, CH₃O), 2.20 (3H, d, ²J_{PCH} = 4 Hz, CH₃P); ³¹P NMR (CDCl₃) δ +114 (¹J_{PW} = 280 Hz).

(S)-(+)-[(O-Methyl)-o-anisylphenylphosphinite] Pentacarbonyltungsten 25. Uncrystallized; [α]_D = +64.4 (c 2.3, CH₂Cl₂); IR (THF) $\bar{\nu}_{\text{CO}}$ cm⁻¹ 2071 (w), 1940 (br, vs); ¹H NMR (CDCl₃) δ 7.70–7.55 (3H, m), 7.5–7.4 (4H, m), 7.15 (1H, dd), 6.9 (1H, dd), 3.4 (3H, d, ³J_{POCH} = 13 Hz, OCH₃); ¹³C NMR (CDCl₃) δ 196.9 (d, ²J_{PWC} = 8.1 Hz, CO(cis)), 132.0 (d, *J*_{PC} = 30 Hz), 132.0, 131.2, 129.6, 128.2 (d, *J*_{PC} = 10 Hz), 121.0 (d, *J*_{PC} = 7.2 Hz), 110.8 (d, *J*_{PC} = 5 Hz), 53.8, 53.7; MS (EI) *m/z* (relative intensity) 572 (18), 570 (25), 542 (39), 514 (9), 486 (59), 430 (63), 383 (13), 247 (100), 183 (55), 107 (34), 91 (23), 77

Scheme 1



(20); MS (EI) isomass calcd for C₁₉H₁₅O₇PW (570) *m/z* (relative intensity), 573 (18), 572 (85), 571 (21), 570 (100), 569 (58), 568 (76); found 573 (20), 572 (76), 571 (27), 570 (100), 569 (55), 568 (70).

(S)-(-)-o-Anisylmethylphenylphosphine Pentacarbonyltungsten 26. Uncrystallized, yellow; TLC *R_f* = 0.51 (9:1 cyclohexane/AcOEt); [α]_D = -77 (c 2.3, CHCl₃); IR (THF) $\bar{\nu}_{\text{CO}}$ cm⁻¹ 2069 (w), 1933 (br, vs); ¹H NMR (CDCl₃) δ 7.6–6.8 (9H, m, arom), 3.66 (3H, s, CH₃O), 2.14 (3H, d, ²J_{PCH} = 6.5 Hz, CH₃P); ¹³C NMR (CDCl₃) δ 197.5 (d, ²J_{PWC} = 7 Hz, CO(cis)), 159.7, 135.5, 132.1, 131.5 (d, *J*_{PC} = 3 Hz), 130.0, 126.6 (d, *J*_{PC} = 41 Hz), 128.5 (d, *J*_{PC} = 10 Hz), 120.9 (d, *J*_{PC} = 8 Hz), 110.9, 54.9 (CH₃O), 21.0 (d, ¹J_{PC} = 29.5 Hz, PCH₃); ³¹P NMR (CDCl₃) δ -10.4 (¹J_{PW} = 237 Hz); MS (EI) *m/z* (relative intensity) 554 (12), 526 (32), 498 (11), 470 (81), 414 (100), 319 (17), 91 (33); HRMS (EI) calcd for C₁₉H₁₅O₆PW [M], 554.0115; found 554.0109; anal. calcd for C₁₉H₁₅O₆PW (554), C, 41.15; H, 2.70; found C, 41.94; H, 2.88.

Results and Discussion

The reaction of the borane complex **2** or **3** with W(CO)₅(THF) (or W(CO)₆) at room temperature or after heating gave poor yields of the corresponding phosphine pentacarbonyltungsten complexes W(CO)₅(PPh₃) **22** or W(CO)₅(C₁₆H₁₈NOP) **23** (<5%).¹⁷

Thus, our strategy toward ligand exchange was modified in order to favor the rupture of the P–B bond. This was achieved

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Table 3. Results of Ligand Exchange between the Amine Pentacarbonyltungsten Complexes **14–20** and the Organophosphorus (P^{III}) Borane **1–3**

entry no.	amine (pK_a)	$W(CO)_5(\text{amine})$	$BH_3(PR_3)$	conditions (solvent; T , $^{\circ}C$)	$W(CO)_5(PR_3)$	yield ^a (%)
1	7 (5.2)	14	1	toluene; reflux	21	40
2	7 (5.2)	14	3	toluene; reflux	23^b	30
3	7 (5.2)	14	3	THF; reflux	23^c	8
4	8 (11.1)	15	1	THF; 60 $^{\circ}C$	21	50
5	8 (11.1)	15	3	THF; 60 $^{\circ}C$	23	8
6	9 (1.8)	16	1	THF; 60 $^{\circ}C$	21	60
7	9 (1.8)	16	3	THF; 60 $^{\circ}C$	23	0
8	10 (0.65)	17	1	THF; 60 $^{\circ}C$	—	—
9	11 (1.3)	18	1	THF; 60 $^{\circ}C$	21	73
10	11 (1.3)	18	3	THF; 60 $^{\circ}C$	23	5
11	12 (1.3)	19	1	THF; 60 $^{\circ}C$	21	87
12	12 (1.3)	19	3	THF; 60 $^{\circ}C$	23	10
13	13 (4.19)	20	1	THF or dioxane; 60 $^{\circ}C$	21	92
14	13 (4.19)	20	2	THF or dioxane; 60 $^{\circ}C$	22	90

^a Isolated yield. ^b $[\alpha]_D = +11.3$ (c 1, $CHCl_3$). ^c $[\alpha]_D = +20.9$ (c 1, $CHCl_3$).

by supplying an amine for the dissociating borane group,¹⁸ instead of CO or THF which form weaker bonds with borane. Moreover, the quantitative substitution of an amine substituent by a phosphine ligand in pentacarbonyltungsten complexes is a well-known reaction.^{12,19} In this case, the facility of the reaction is directly related to the basicity of the coordinated amine ligand, with a good correlation between the decreasing rate of substitution and the increasing pK_a values of the amine. The rupture of the amine-metal bond is the rate determining step for these substitution reactions, and for this reason the kinetics give an idea of the strength of the W–N bond.^{12a}

Here, the substitution reaction is not quite the same because the free P^{III} compound must be generated by a tandem reaction, involving the complexation of the borane group by the amine ligand (Scheme 1). We emphasize here that an amine with a low pK_a increases the possibility of its dissociation from the tungsten complex, while the removal of the borane group should be favored by an amine with a high pK_a . Consequently, in view of these opposing factors, the ligand exchange was studied with a variety of amine pentacarbonyltungsten complexes **14–20** (Scheme 1; Table 3). Examination of the results in Table 3 shows that the pyridine pentacarbonyltungsten **14** reacts with the diphenylmethylphosphineborane **1** in refluxing toluene, to give the complex **21** with 40% yield (entry 1). This is already an improvement over the reaction with $W(CO)_5(THF)$ mentioned above.¹⁷ Under the same conditions, $W(CO)_5(py)$ **14** also reacts with oxazaphospholidine borane **3** to give complex **23** in a 30% yield (entry 2). The optical activity ($[\alpha]_D = +11.3$) and the 1H NMR analysis of the chiral complex **23**, obtained in refluxing toluene (entry 2), indicate partial epimerization of the oxazaphospholidine ligand.²⁰ This can be explained by the inversion of configuration at the chiral P center, owing to the permutation of the phenyl and $W(CO)_5$ groups, bringing the latter group in opposite position to the substituents of the ring.²¹ Unfortunately, the yield of **23** decreased to 8% under milder conditions (refluxing THF), even though a better diastereoselectivity was obtained (entry 3). When the piperidine complex **15** was used for the ligand exchange with **1** or **3**, the phosphine pentacarbonyltungsten complexes **21** and **23** were obtained with

yields of 50 and 8%, respectively (entries 4 and 5). Better results were obtained when the diamine ligands benzo[c]-cinnoline, phenylpyrimidine, and especially pyrimidine were used, because the phosphine pentacarbonyltungsten complex **21** was isolated in yields ranging from 60 to 87% (entries 6, 9, and 11). However, the same efficiency was not observed for the formation of the chiral complex **23**, which was obtained in very low yields (0–10%) (entries 7, 10, and 12). $W(CO)_5\text{-(pyz)}$ **17** undergoes quantitative ligand substitution with free phosphines at room temperature but does not react with the phosphine boranes even by heating at 60 $^{\circ}C$ (entry 8). The facility of substitution of $W(CO)_5(\text{pyz})$ **17** indicates that the W–N bond is relatively weak, but at the same time the pK_a (0.65) for pyrazine is too low for borane group removal from the phosphine borane complex. Moreover, this complex is thermally unstable and decomposes rapidly at 60 $^{\circ}C$. Finally, the use of the complex **20** bearing the piperazine ligand ($pK_a = 4.19$), permits efficient exchange with the phosphine boranes **1–6** in THF or dioxane at 60 $^{\circ}C$ (Tables 3 and 4). Under these conditions, the corresponding phosphine pentacarbonyltungsten complexes **21** and **22** were obtained from **1** and **2**, in yields of 90 and 92%, respectively (Table 3, entries 13 and 14).

Another interesting aspect of the exchange reactions, is the formation of a white insoluble powder **27** when the amine complexes **18–20** are used (Scheme 1). These insoluble white powders do not melt but decompose between 200 and 220 $^{\circ}C$, and their IR spectra exhibit strong bands at 800 and 1300 cm^{-1} which are characteristic of the presence of B–N bonds.²²

The efficiency of ligand exchange with piperazine pentacarbonyltungsten **20** is demonstrated by the preparation of chiral complexes **23–26** from the borane adducts **3–6** in yields of 63–90% (Table 4, entries 1–4). It is also of great interest that the optical activity²⁰ and the 1H NMR analysis of the oxazaphospholidine complex **23** indicate no detectable epimerization (entry 1). These results also prove that the mechanism of ligand exchange occurs with retention of configuration at the chiral P

- (17) The exchange reaction between the complex **2** and $W(CO)_5(THF)$ was mentioned by P. Pellon, Y. Gourdél, and M. Le Corre at the "Journées de Chimie Organique de SFC", Palaiseau, France in September 1992 and reexamined by us.
- (18) (a) Baldwin, R. A.; Washburn, R. M. *J. Org. Chem.* **1961**, 26, 3549–3550. (b) Pelter, A.; Smith, K. Boron–Nitrogen Compounds. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: New York, 1979; Vol. 3, pp 925–940.
- (19) Howell, J. A.; Burkinshaw, P. M. *Chem. Rev.* **1983**, 83, 557–599.

- (20) A sample of the enantiomer of the complex **23** ($[\alpha]_D = -32.1$; c 5, $CHCl_3$) has been prepared according to the procedure described in refs 1c and 7, by reaction of $W(CO)_5(THF)$ with (2*R*,4*S*,5*R*)-(+)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine derived from (–)-ephedrine.
- (21) The epimerization of this heterocycle during quaternization has already been observed; see: Jugé, S.; Wakselman, M.; Stephan, M.; Genêt, J. P. *Tetrahedron Lett.* **1990**, 31, 4443–4444.
- (22) The formation of oligomers and eventually polymers by heating diborane and piperazine together has been described (Burg, A. B.; Iachia, B. *Inorg. Chem.* **1968**, 7, 1670–1672) and prepared by reaction of $W(CO)_5(THF)$ with the enantiomerically pure (*R*)-(+)-*o*-anisylmethylphenylphosphine derived from (+)-ephedrine.^{1c}

Table 4. Results of the Ligand Exchange between the Piperazine Pentacarbonyltungsten Complexes **20** and the Chiral Organophosphorus (P^{III}) Boranes **3–6**

entry no.	$BH_3(PR_3)$	abs. conf.	react. time ^a	$W(CO)_5(PR_3)$	yield ^b (%)	abs. conf. product
1	3	(-)-(2 <i>S</i> ,4 <i>R</i> ,5 <i>S</i>)	72 h	23	63	(+)-(2 <i>R</i> ,4 <i>R</i> ,5 <i>S</i>) ^c
2	4	(+)-(R)	168 h	24	65	(+)-(S) ^d
3	5	(+)-(S)	48 h	25	90	(+)-(R) ^e
4	6	(-)-(R)	24 h	26	80	(-)-(S) ^f

^a All essays were realized in THF (or dioxane) at 60 °C. ^b Isolated yield. ^c Reference 20. ^d $[\alpha]_D = +4.6$ (c 1.1, CH_2Cl_2). ^e $[\alpha]_D = +64.4$ (c 2.3, CH_2Cl_2). ^f $[\alpha]_D = -77$ (c 2.3, $CHCl_3$).

center. The high stereoselectivity has been confirmed by the reaction between the piperazine complex precursor **20**, and the (*R*)-(+)-*o*-anisylmethylphenylphosphine borane (PAMP· BH_3) **6**, which gives the first example of an optically pure (*S*)-PAMP pentacarbonyltungsten complex **26** (entry 4). On this basis, we can reasonably believe that the absolute configurations of the phosphinite pentacarbonyltungsten complexes **24** and **25** (dextrogyre) must be *S* and *R*, respectively (entries 3 and 4).

It also appears that the reactions with the oxazaphospholidine and the phosphinite borane **3**, **4**, require longer reaction times and give the lowest yields of the borane complexes studied (Tables 3 and 4). The efficiency of the exchange could be related to the strength of the B–P bond, which depends on the basicity and on the Tolman cone angle of the phosphorus compounds.^{23,24}

(23) Tolman, C. A. *Chem. Rev.* **1977**, 77, 313–348.

(24) For the influence of σ donor character or basicity of $P(III)$ organophosphorus ligands toward borane complex, see: (a) Lines, E. L.; Centofanti, L. F.; Hafler, D. A. *Phosphorus* **1974**, 5, 5–7. (b) Alford, K. J.; Bishop, E. O.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **1976**, 920–922. For empiric rules on the donor–acceptor properties of phosphorus ligand, see: (c) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, 92, 2953–2956.

In conclusion, the first efficient method giving chiral and achiral phosphine pentacarbonyltungsten complexes has been achieved from a ligand exchange reaction between amine $W(CO)_5$ and a phosphine borane. The piperazine pentacarbonyltungsten $W(CO)(pipz)$ **20** was found to be the best precursor, affording the corresponding chiral and achiral phosphorus complexes in high yields (63–92% yields). The stereochemistry of this reaction proceeds with retention of configuration at the chiral P center and high stereoselectivity, permitting the preparation of new optically active organophosphorus pentacarbonyltungsten complexes. It is noteworthy that this method is of particular interest, because the isolation of the organophosphorus compounds in tricoordinate form is not necessary. The mechanism of ligand exchange²⁵ and the principle strategy for the preparation of complexes with other transition metals are currently under investigation.

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