Optically Active Phospholes: Synthesis and Use as Chiral Precursors for Phosphinidene and Phosphaferrocene Complexes

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Phospholes bearing chiral menthyl, myrtanyl, and (4-isopropyloxazolino)phenyl groups at the phosphorus atom were prepared. They were used as precursors for 7-phosphanorbornadienes and phosphinidene complexes. Unexpectedly, the [(4-isopropyloxazolino)phenyl]phosphinidene gave an intramolecular adduct with the imine moiety, which behaved as a 1,3-dipole in cycloaddition reactions. This afforded a new, general approach to 7-aza-1-phosphanorbornadiene and norbornene derivatives. The (4-isopropyloxazolino)phenyl-substituted phosphole was also used for the synthesis of new chiral phosphaferrocene complexes bearing oxazoline moieties.

Introduction

The organic chemistry of phospholes is extremely rich and varied, as has been shown by the work of many groups during the last decades.[1] Besides simple modifications of the phosphole ring substituents, three main transformations giving access to other classes of phosphorus derivatives are known: these are [4+2] cycloaddition reactions at the dienic system, which afford 7-phosphanorbornenes[2,3] or 7-phosphanorbornadiene[4] derivatives; [1,5] sigmatropic shifts of the aryl, vinyl, or other labile phosphorus substituents around the phosphole nucleus, which lead to 1-phosphanorbornadienes;[5] and finally, the reactivity of either phospholes themselves or phospholyl anions towards suitable transition metal derivatives, which affords an easy access to phosphacyclopentadienyl complexes and phosphametallocenes.[6,7]

Despite the wide synthetic potential of phosphole chemistry, the use of chiral species as synthetic tools has barely been considered. A few optically active phospholes, mainly dibenzophosphole derivatives, have been applied as chiral auxiliaries in transition metal promoted reactions.[8] Recent reports from T. Hayashi disclose the synthesis of enantiomerically pure 2,5-dimenthyl-1-phenylphosphole and its use for the preparation of phosphaferrocene, phosphacymantrene, and diphosphole derivatives.[9]

According to an analogous strategy, i.e. taking advantage from the reactivity of nonracemic phospholes to prepare chiral phosphanes with nonconventional structures and potential interest in catalysis, we started the work presented herein. This includes the synthesis of some new chiral phospholes and their use as precursors for phosphirenes, phosphaferrocenes, and new azaphosphanorbornadiene derivatives.

Results and Discussion

Synthesis of Chiral Phospholes

Chirality in phospholes could be provided by optically pure substituents on either the carbon or the phosphorus atoms. The phosphole ring itself has a low phosphorus inversion barrier (ca. 16 kcal/mol), so it racemizes at room temperature. From a synthetic point of view, the most attractive compounds seem to be phospholes bearing a chiral group on the phosphorus atom, whose easy preparation from phospholyl anions and chiral electrophiles contrasts with the restricted availability of optically active diene moieties.

In this work, two kinds of chiral auxiliaries were considered as phosphorus substituents: alkyl groups derived from chiral pool terpene alcohols (menthol and myrtanol), and valine-derived phenyloxazoline moieties. Both terpene alcohols and amino acids can be conveniently used as stoichiometric chiral auxiliaries because of their large-scale availability.

Chiral phospholes are obtained from 3,4-dimethyl-1-phenylphosphole (**1**)[10] via the corresponding phospholyl anion by substitution on the phosphorus atom, as shown

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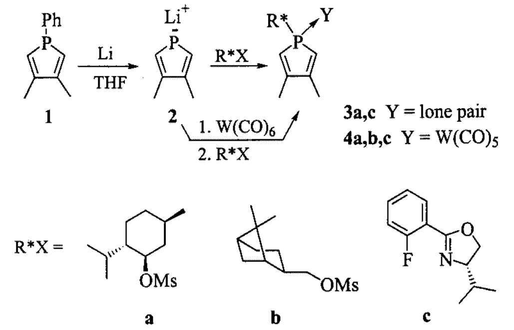
in Scheme 1. After cleavage of the phosphorus−phenyl bond of **1** with lithium, the phospholyl anion **2** gives nucleophilic substitution reaction on the mesylate of (−)-menthol to afford the *P*-neomenthyl-substituted phosphole **3a**.

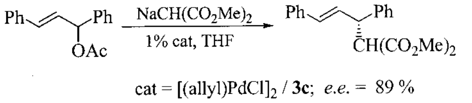


Scheme 1. Synthesis of chiral phospholes

The analogous reaction between the phospholyl anion and the mesylate of (1*S*)-myrtanol[11,12] afforded the corresponding, highly air-sensitive *P*-myrtanylphosphole compound. It was isolated only as its $W(CO)_5$ complex **4b**.

Reaction of **2** with the (−)-(*S*)-2-(2-fluorophenyl)-4-isopropyloxazoline gave the air-stable phosphole **3c** in good yield (61%). The (fluorophenyl)oxazoline has already been used as an electrophile in the analogous *P*-arylation of a dibenzophospholyl anion.[8e]

The optically active phospholes **3a** and **3c** provide new chiral ligands for transition metal promoted asymmetric catalysis. Their potential applications are likely to be those where other phospholes have already been used successfully: for example hydroformylation, hydrogenation, and carbonylation reactions. Moreover, phosphole **3c** should find applications in a number of catalytic reactions usually promoted by phosphanyloxazoline ligands.[13] As a very preliminary test, we checked the effectiveness of phosphole **3c** as chiral ligand in the palladium-catalyzed substitution of 1,3-diphenylpropenyl acetate with sodium malonate under standard conditions. As expected, the observed catalytic activity, as well as the enantioselectivity, is quite satisfactory (Scheme 2).

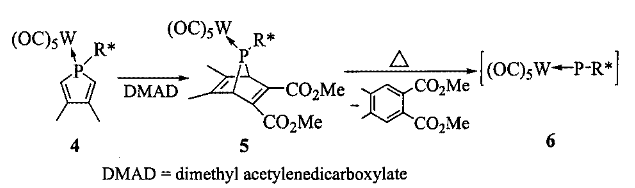


Scheme 2. Palladium-catalyzed allylic substitution

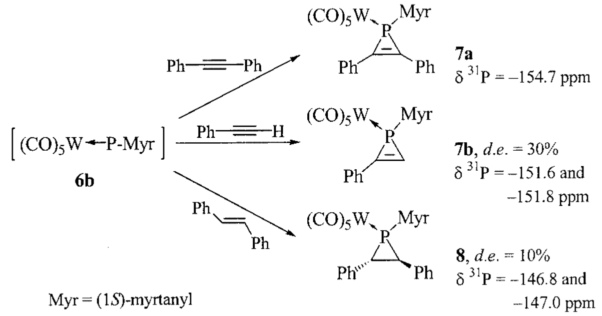
Exhaustive catalytic screening of phospholes **3** lies beyond the scope of this work and will be reported later. Indeed, the main purpose of this work was to check the use of phospholes **3** as chiral intermediates for the synthesis of new phosphorus derivatives through either Diels−Alder cycloaddition reactions on the dienic system or [1,5] sigmatropic shifts of the aryl moiety of **3c**. Results are given hereafter.

Synthesis of (7-Phosphanorbornadiene)W(CO)$_5$ Complexes − Generation of Chiral Phosphinidenes

(7-Phosphanorbornadiene)W(CO)$_5$ complexes are easily accessible from the corresponding phosphole complexes by Diels−Alder cycloadditions with activated alkynes.[4] These compounds were mainly used as synthetic precursors for terminal phosphinidene complexes, which are highly reactive intermediates with carbene-like behavior.[14,15] For instance, addition of (phosphinidene)M(CO)$_5$ complexes to olefins and alkynes leads to the corresponding phosphirane and phosphirene complexes, respectively. When the phosphinidene phosphorus atom bears an optically pure substituent, chiral induction can be expected in its addition to unsymmetrical olefins and acetylenes. To verify this theory, we examined the preparation of the 7-phosphanorbornadiene complexes **5**, as well as their thermolysis and the subsequent phosphinidene trapping reactions, as shown in Schemes 3 and 4.



Scheme 3. Generation of phosphinidene complexes



Scheme 4. Trapping reactions of transient phosphinidene complexes

The phosphole complexes **4a−c** could be obtained by treating the preformed phospholes **3** with the (THF)W(CO)$_5$ complex. For the air-sensitive phosphole **3b**, the most convenient procedure[16] included complexation of the phospholyl anion, followed by reaction of the phospholyltungsten complex with myrtanyl mesylate to give **4b** (see Exp. Sect.).

The course of the reaction between **4** and DMAD was largely dependent on the nature of the phosphorus substituent R*. When R* = neomenthyl, the Diels−Alder cycloaddition was prevented by the steric hindrance of the phosphorus substituent. When R* = myrtanyl, the steric hindrance around the phosphorus atom was greatly reduced and the Diels−Alder reaction with DMAD leads to the expected 7-phosphanorbornadiene **5b**, which was isolated and fully characterized.

The generation and trapping of the pentacarbonyl(*P*-myrtanylphosphinidene)tungsten complex from **5b** was checked in small-scale experiments by ^{31}P NMR spectroscopy on crude reaction mixtures (Scheme 4). Diphenylacetylene, phenylacetylene, and *trans*-stilbene were used as trapping reagents because, in such cases, the anticipated complexed phosphirene and phosphirane products should give very characteristic ^{31}P NMR signals at high-field shifts.[14,17]

These experiments show that thermolysis of **5b** under the usual experimental conditions,[14,17] affords the pentacarbonyl(*P*-myrtanylphosphinidene)tungsten complex **6b**, which displays the expected electrophilic behavior toward olefins and alkynes. Phosphirane and phosphirene complexes are obtained as the only reaction products, by [2+1] cycloaddition reactions.

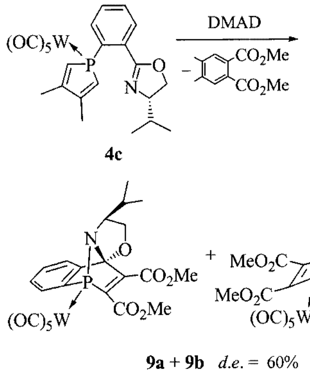
In the case of unsymmetrical alkynes and olefins, chiral induction from the optically active myrtanyl substituent should give diastereoselective addition reactions. Unfortunately, mixtures of diastereomers, with rather poor diastereomeric excesses, are obtained upon cycloaddition of **6b** with phenylacetylene and *trans*-stilbene, leading to **7b** and **8**, respectively. To be stereoselective, the reaction with phenylacetylene requires diastereoselective formation of a chiral phosphorus center, while the diastereoselective addition of **6b** on *trans*-stilbene requires enantiofacial selectivity. The low efficiency of the myrtanyl group as chiral auxiliary in both these reactions is probably due to the presence of the flexible CH_2 spacer between the phosphorus atom and the chiral centers of the myrtanyl moiety. The diastereoselectivity is likely to be improved by using chiral auxiliaries bearing stereogenic centers closer to the phosphorus atom.[18]

Finally, trapping reactions of the *P*-myrtanylphosphinidene **6b** should give a convenient access to optically pure phosphirane[19] and phosphirene derivatives, but only when symmetrically substituted unsaturated substrates are used, as shown by the synthesis of **7a**. Otherwise, separation of the diastereomeric mixtures would be required.

Given that several procedures are known for removing phosphirenes and phosphiranes from their pentacarbonyltungsten or -molybdenum complexes,[20−22] reactions in Scheme 4 should represent new potential sources of chiral ligands for enantioselective catalysis.

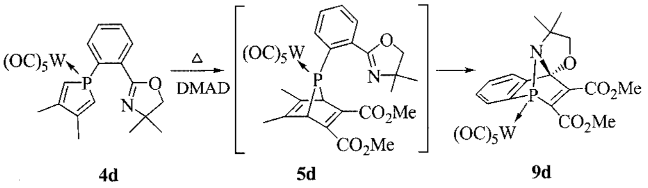
In the reaction of the phosphole complex **4c** {R* = 2-[(*S*)-4-isopropyloxazolino]phenyl} with DMAD, the expected 7-phosphanorbornadiene derivative **5c** was not detected. Nevertheless, a clean reaction occurred to give a new phosphorus derivative as a mixture of two isomers. Spectroscopic data and NMR analysis of the crude reaction mixture showed formation of dimethyl phthalate. This suggests that the Diels−Alder reaction took place as expected, but that the 7-phosphanorbornadiene complex decomposed instantaneously to generate the corresponding phosphinidene **6c** (Scheme 3). The excess DMAD was suspected to be the trapping reagent for the intermediate phosphinidene.

This hypothesis is supported by spectroscopic analysis of the pure final product, which was in agreement with the bicyclic structure **9** shown in Scheme 5. Nevertheless, an unambiguous assignment was prevented by the presence of the two inseparable isomers **9a** and **9b**, in a 4:1 ratio.



Scheme 5. Reaction of the {3,4-dimethyl-1-[2-(4-isopropyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]phosphole}W(CO)$_5$ complex **4c** with dimethyl acetylenedicarboxylate

To confirm the structural assignment, we decided to perform the same reaction starting from the achiral (oxazolylphenyl)phosphole complex **4d**, which should lead to a single isomer of the final product and thus facilitate its purification and characterization (Scheme 6).



Scheme 6. Reaction of the {3,4-dimethyl-1-[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]phosphole}W(CO)$_5$ complex **4d** with dimethyl acetylenedicarboxylate

The expected reaction between the phosphole complex **4d** and DMAD led to the 7-aza-1-phosphanorbornadiene **9d**, which was easily isolated and fully characterized. An X-ray diffraction study of **9d** confirmed the proposed structure (Figure 1).

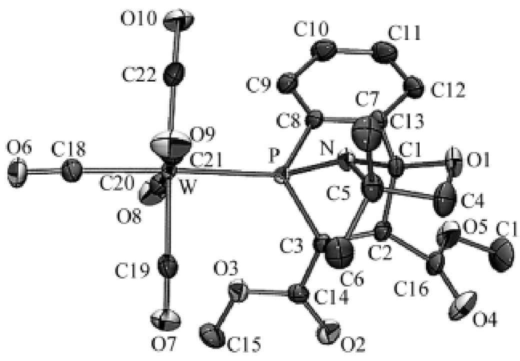
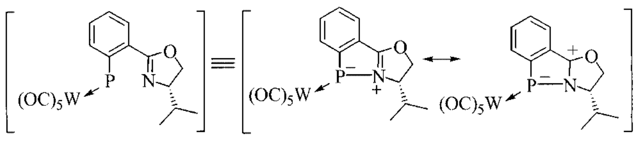


Figure 1. ORTEP diagram for complex **9d**; selected bond lengths [Å]: W−P 2.4495(7), P−N 1.707(2), P−C(8) 1.845(3), P−C(3) 1.890(3), N−C(1) 1.474(3); selected bond angles [°]: P−W−C(18) 172.13(9), C(3)−P−C(8) 94.4(1), P−N−C(1) 100.0(2), C(1)−N−C(5) 106.9(2), O(1)−C(1)−N 106.1(2)

To date, only one example of a 7-aza-1-phosphanorbornadiene has been reported,[23] which was obtained by trapping a (pentamethylcyclopentadienyl)phosphinidene complex with a nitrile. The first formed adduct rearranges through a [4+2] cycloaddition to give the norbornadiene.

In the reactions of Schemes 5 and 6, formation of the 7-aza-1-phosphanorbornadiene complexes **9** can be explained as follows. The [4+2] cycloaddition between **4c** (or **4d**) and excess DMAD gives the 7-phosphanorbornadiene complex **5c** (or **5d**), which instantaneously generates the corresponding phosphinidene complex. The easy decomposition of these 7-phosphanorbornadiene complexes can be explained by the intramolecular interaction between the phosphorus atom and the nitrogen lone pair of the oxazoline moiety, as it has already been shown that amines and strongly basic phosphanes catalyze such reactions.[24] The phosphinidene complex is thus generated as an adduct between the imine nitrogen atom and the electron-deficient phosphorus atom, which can be described by the two resonance structures **I** and **II** in Scheme 7.



6c **I** **II**

Scheme 7. {*P*-[2-(4-Isopropyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]-phosphinidene}W(CO)$_5$ complex **6c**

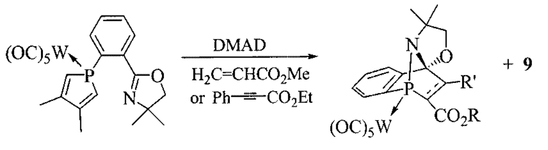
Structure **II** clearly emphasizes the 1,3-dipolar nature of the adduct and explains its [3+2] cycloaddition with DMAD leading to **9**. The reaction intermediate of Scheme 7, can be considered as a phosphaazomethine ylide.

As far as we know, phosphinidene−imine adducts have never been described before. However, other P/N adducts are known. A pyrazolyl−phosphinidene complex has been reported by Cowley. In this case, the coordination of the nitrogen lone pair substantially reduced the electrophilicity of the phosphinidene, thus permitting its isolation.[25] Phosphinidene−nitrile adducts have been generated as reactive intermediates and their reactivity in 1,3-dipolar cycloadditions has been studied by Streubel.[26−28]

Azomethine ylides,[29] as well as (iminomethylene)phosphoranes and analogs[30] were found to be useful as synthetic building blocks through [3+2] cycloadditions. Thus, the use of the phosphaazomethine ylides above as synthetic tools can be envisaged.

Results given in Schemes 5 and 6 point out the strongly nucleophilic behavior of the (2-oxazolylphenyl)phosphinidene complexes, which contrasts with that of simple alkyl- or aryl-substituted pentacarbonyl(phosphinidene)tungsten complexes. Further experiments showed that the [3+2] cycloaddition with DMAD took place preferentially even in the presence of excess diphenylacetylene, an usually efficient phosphinidene trapping reagent.

Preliminary tests (^{31}P NMR analysis of crude reaction mixtures) show that electron-deficient olefins and alkynes other than DMAD can be used as trapping reagents (Scheme 8). In the presence of methyl acrylate (or ethyl phenylpropionate), diastereomeric mixtures of the bicyclic derivatives **10a** (or **10b**) were obtained. However, complex **9** is still formed in some amount (**10/9** ≈ 80:20), even when a threefold excess of the trapping reagent was used, showing that DMAD competes well with the other reagents. The whole reaction sequence can be improved by using ethyl phenylpropionate as the only cycloaddition partner for both the Diels−Alder reaction on phosphole **4d** and the phosphinidene trapping. Under such conditions, the crude reaction mixture contains complex **10** as the major product.



4d

10a R = Me, R' = H
10b R = Et, R' = Ph

Scheme 8. Reactivity of the {3,4-dimethyl-1-[2-(4,4-dimethyl-4,5-dihydro-1,3-oxazol-2-yl)phenyl]phosphole}W(CO)$_5$ complex **4d**

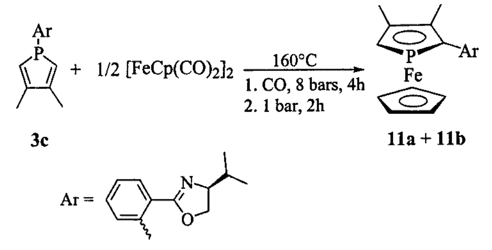
To summarize, the cycloaddition reactions shown in Schemes 6 and 8 demonstrate the generation of new phosphinidene intermediates, which display an unprecedented 1,3-dipolar behavior. Their reactivity allows the synthesis of new tricyclic 7-aza-1-phosphanorbornadiene derivatives.

Application of such reactions to the preparation of new optically pure ligands for transition metal catalysis should be possible, provided that the separation of the diastereoisomers of **9** (or **10**) and the removal of the azaphosphanorbornadienes from their tungsten complexes could be performed. Although 7-aza-1-phosphanorbornadienes are new compounds whose catalytic properties are difficult to predict, the use of 1-phosphanorbornadienes as auxiliaries in transition metal catalysis, including asymmetric catalysis, is already well documented.[31]

Studies on the synthetic applications of the 1,3-dipolar cycloadditions above are in progress.

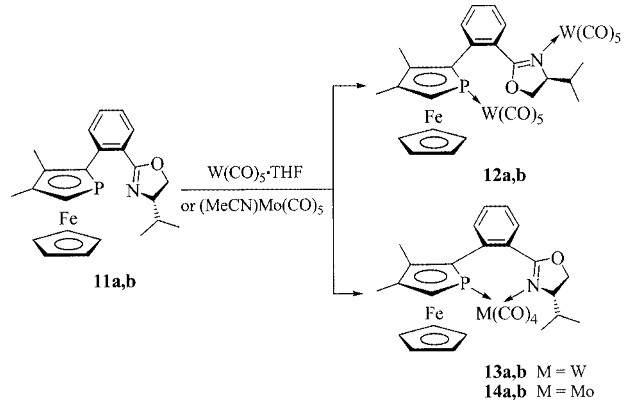
Synthesis of Chiral Phosphaferrocene Derivatives

Phosphaferrocenes[32] are usually obtained from phospholes by two different procedures: 1) lithium-induced cleavage of the phosphorus substituent and reaction of the phospholyl anion with either iron halides[33,34] or arene(cyclopentadienyl)iron derivatives;[35] and 2) thermal [1,5] sigmatropic shift of the phosphorus substituent and subsequent trapping of the intermediate 2*H*-phosphole by suitable iron complexes.[36,37] The second approach was selected for the synthesis of phosphaferrocenes starting from phosphole **4c** and [CpFe(CO)$_2$]$_2$ (Scheme 9).



Scheme 9. Synthesis of the phosphaferrocene derivatives **11**

Under the usual reaction conditions, the aryl group of **4c** underwent a [1,5] sigmatropic shift, followed by deprotonation of the 2*H*-phosphole and complexation to the cyclopentadienyliron moiety to afford **11** as a mixture of two isomers in a 1:2 ratio and in a moderate yield. The α-substituted phosphaferrocenes display planar chirality, so the formation of two diastereoisomers was expected. Chiral induction from the oxazoline moiety favors one of them, but the diastereoselectivity level is not yet satisfactory.



Scheme 10. Tungsten and molybdenum complexes of the phosphaferrocene **11**

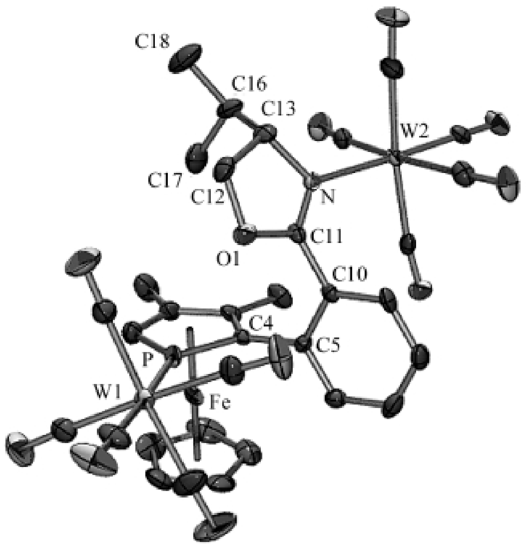


Figure 2. ORTEP diagram for the tungsten complex **12a**; selected bond lengths [Å]: W(1)−P 2.462(2), W(2)−N 2.284(5), Fe−P 2.253(2); selected bond angles [°]: C(1)−P−C(4) 91.8(3), C(11)−N−C(13) 107.7(5), W(2)−N−C(11) 130.0(4), W(2)−N−C(13) 122.2(4)

Purification of the final products **11** and separation of isomers, proved to be difficult because of their air sensitivity. Thus, complexation of the phosphaferrocenes by pentacarbonyltungsten or -molybdenum was envisaged and furnished stable, easily isolable species (Scheme 10).

The main product obtained by reaction of **11** with an excess of the tungsten complex (THF)W(CO)$_5$, was the dimetallic complex **12**, where both the phosphorus and nitrogen atoms are complexed by a W(CO)$_5$ group. The major

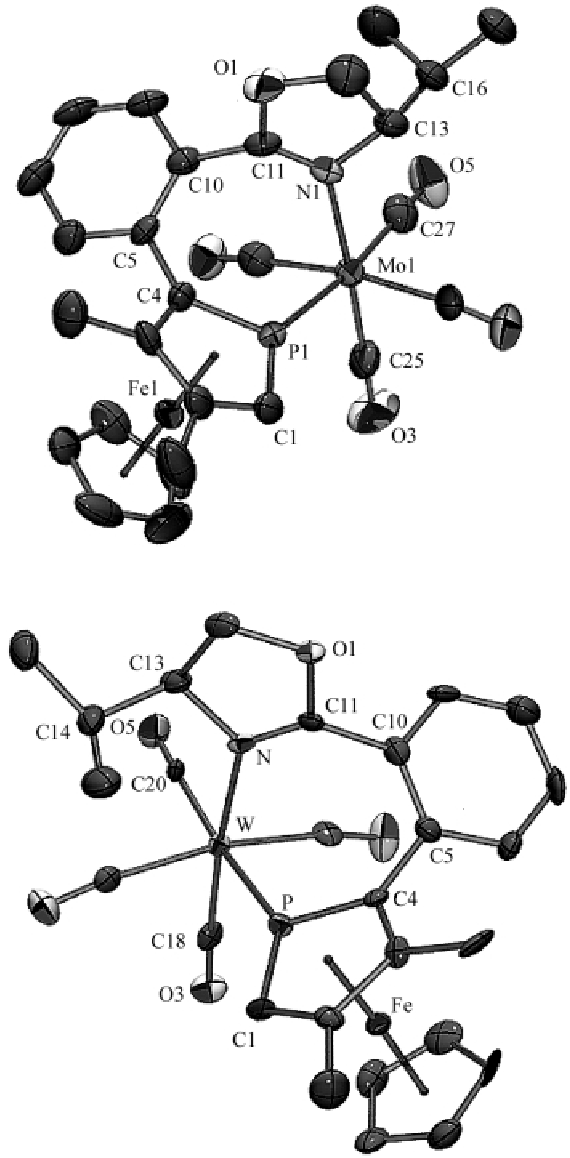


Figure 3. ORTEP diagrams for the molybdenum and tungsten complexes **14a** and **13b**; selected bond lengths [Å]: **14a**: Mo−P 2.475(1), Mo−N 2.277(4), Fe−P 2.240(2); **13b**: W−P 2.425(3), W−N 2.274(8), Fe−P 2.231(3); selected bond angles [°]: **14a**: P−Mo−N 79.4(1), C(1)−P−C(4) 90.6(3), C(11)−N−C(13) 106.9(4), Mo−N−C(11) 130.1(4), Mo−N−C(13) 122.6(3); **13b**: P−W−N 79.5(2), C(1)−P−C(4) 91.9(5), C(11)−N−C(13) 107.7(8), W−N−C(11) 128.4(7), W−N−C(13) 123.8(6)

diastereomer, (*S*,*S*)-**12a** (M = W), was obtained in pure form after crystallization. Its structure was confirmed by X-ray crystallography, as shown in Figure 2.

Minor amounts of the chelate derivative **13** (M = W) were also present in the reaction mixture. Crystals of one diastereomer (**13b**) were isolated and analyzed by X-ray crystallography (Figure 3, bottom). Its absolute configuration was determined as (*S*,*S*).

In the reaction with the molybdenum complex (THF)Mo(CO)$_5$, the P,N-bidentate phosphaferrocene **11** exclusively formed the chelate derivative **14** (M = Mo) as an isomeric mixture. The main isomer was obtained in pure form after crystallization and was characterized by X-ray diffraction studies. The ORTEP drawing for **14a** as well as selected bond angles and distances are given in Figure 3 (top). From the X-ray data, an (*R*,*S*) absolute configuration can be assigned to the isolated complex.

Isolation of complexes **13** and **14** shows that the geometry of the P,N-bidentate ligand **11** is suitable for chelate formation. This is a key feature of the ligand, as far as its use as a chiral auxiliary in catalysis is concerned. The high catalytic efficiency of oxazolines coupled with phosphanylferrocene moieties is well established to date,[38] and the use of phosphaferrocenes in catalysis is a field of growing interest.[39] Thus, ligands **11**, which associates the phosphaferrocene and the oxazoline moieties, should find interesting applications in organometallic asymmetric catalysis. Nevertheless, improvement of the synthetic approach and an efficient separation procedure for the two diastereomers **11a** and **11b** is required.

An alternative synthetic approach to the phosphaferrocenes **11** and other metallocene analogs could be the formation of the corresponding phospholylpotassium derivative after [1,5] shift of the aryl group.[40] The phospholyl anion could be treated with various metal halide complexes under milder conditions, and would hopefully be more diastereoselective in its outcome.

Conclusion

This work shows that phospholes bearing various optically pure substituents at the phosphorus atom are easily accessible species. They can either be applied as chiral auxiliaries in asymmetric transition metal catalysis or used as versatile synthons. As a very preliminary study, we have shown here that chiral phosphinidene complexes and phosphaferrocene derivatives can be obtained from these phospholes. The (oxazolylphenyl)phosphole **3c** seems to be a particularly promising starting material. On one hand, an unprecedented, [1,3]-dipole-like reactivity of the corresponding terminal phosphinidene complex has been demonstrated, and on the other hand, phosphole **3c** underwent a [1,5]-sigmatropic shift of the phosphorus substituent and should allow application of the well-known 2*H*-phosphole chemistry to the asymmetric synthesis of phosphorus derivatives.

Experimental Section

General: All reactions were routinely performed under nitrogen by using Schlenk technique and dry deoxygenated solvents. NMR spectra were obtained at 25 °C with a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C, and 81.01 MHz ^{31}P. Chemical shifts are expressed in ppm downfield from external TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P), and coupling constants are given in Hz. Mass spectra were obtained at 70 eV with an HP 5989 B spectrometer coupled with an HP 5890 chromatograph by the direct inlet method. IR spectra were obtained with a Perkin−Elmer 297. Elemental analyses were performed by the Service d'Analyse du CNRS at Gif sur Yvette, France.

1-(2-Isopropyl-5-methylcyclohexyl)-3,4-dimethylphosphole (3a): A solution of lithium 3,4-dimethylphospholide in 30 mL of THF was prepared by treating 3,4-dimethyl-1-phenylphosphole (3 g, 16 mmol) with excess lithium at room temperature. Menthyl mesylate (3.7 g, 16 mmol) was added, and the solution was allowed to reflux for 1 h. After hydrolysis, evaporation of THF, and extraction of the aqueous layer with diethyl ether, the organic phase was dried with $MgSO_4$. The product was purified by chromatography on silica gel with hexanes, affording **3a** as a colorless oil. Yield: 25% (1.0 g). ^{31}P NMR (CDCl$_3$): δ = −3.0. ^{1}H NMR (CDCl$_3$): δ = 0.85 (d, $^3J_{H,H}$ = 6.1 Hz, 3 H, Me), 0.94 (d, ^3J = 6.4 Hz, 3 H, Me), 0.95 (d, ^3J = 6.5 Hz, 3 H, Me), 1.04−1.99 (m, 9 H), 2.08 [s, 3 H, C(CH$_3$)], 2.09 [s, 3 H, C(CH$_3$)], 2.56 (m, 1 H), 6.41 (d, $^2J_{P,H}$ = 36.9 Hz, 2 H, 2-H and 5-H). ^{13}C NMR (CDCl$_3$): δ = 17.75 (Me), 17.81 (Me), 21.2 (Me), 21.5 (Me), 22.7 (Me), 26.5 (d, *J* = 8.7 Hz, CH$_2$), 28.7 (d, *J* = 6.1 Hz, CH), 31.2 (d, *J* = 7.8 Hz, CH), 36.1 (CH$_2$), 38.8 (d, *J* = 4.6 Hz, CH), 42.6 (CH$_2$), 48.8 (d, *J* = 11.6 Hz, CH), 129.1 (CH=), 146.5 (CH=), 146.7 (s, C).

(*S*)-2-[2-(3,4-Dimethyl-1*H*-phosphol-1-yl)phenyl]-4-isopropyl-4,5-dihydro-1,3-oxazole (3c): A mixture of lithium 3,4-dimethylphospholide (96 mmol), prepared from lithium metal and 3,4-dimethyl-1-phenylphosphole (18.0 g, 96 mmol), and (*S*)-2-(2-fluorophenyl)-4-isopropyl-4,5-dihydrooxazole (14.8 g, 72 mmol) in THF was heated at 45 °C for 48 h. After hydrolysis and extraction of the aqueous layer with diethyl ether, the organic phase was dried with $MgSO_4$. After evaporation of the solvent, the residue was purified by chromatography on silica gel with a hexane/ether (95:5) mixture, giving **3c** as a colorless oil. Yield: 61% (13.0 g). ^{31}P NMR (CDCl$_3$): δ = 0.9. ^{1}H NMR (CDCl$_3$): δ = 0.99 [d, *J* = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.10 [d, *J* = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$], 1.87 [m, *J* = 6.6 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.10 (d, $^4J_{P,H}$ = 4.2 Hz, 6 H, CH$_3$), 4.29 (m, 3 H, CHN and OCH$_2$), 6.62 (d, $^2J_{P,H}$ = 34.3 Hz, 2 H, P−CH), 7.24−7.31 (m, 2 H, Ar-H), 7.35−7.41 (m, 1 H, Ar-H), 7.79−7.86 (m, 1 H, Ar-H). ^{13}C NMR (CDCl$_3$): δ = 17.8 (d, ^3J = 2.3 Hz, 2 CH$_3$), 18.7 [CH(*C*H$_3$)$_2$], 19.1 [CH(*C*H$_3$)$_2$], 33.1 [*C*H(CH$_3$)$_2$], 70.4 (OCH$_2$), 73.5 (CHN), 127.6 (CH), 128.9 (d, *J* = 13.8 Hz, CH), 129.1 (CH), 130.4 (CH), 130.7 (d, ^2J = 18.6 Hz, C), 133.5 (CH), 136.4 (d, ^1J = 21.4 Hz, C), 147.7 (d, ^2J = 9.5 Hz, C), 147.9 (d, ^2J = 10.5 Hz,), 162.8 (C=N). MS: *m*/*z* (%) = 299 (78) [M$^+$], 230 (100). $C_{18}H_{22}NOP$ (299.35): calcd. C 72.22, H 7.41, N 4.68; found C 71.88, H 7.54, N 4.51. [α]$_D$ = +64 (*c* = 1, toluene).

2-[2-(3,4-Dimethyl-1*H*-phosphol-1-yl)phenyl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole (3d): A mixture of lithium 3,4-dimethylphospholide (48 mmol), prepared from lithium metal and 3,4-dimethyl-1-phenylphosphole (9.0 g, 48 mmol), and 2-(2-fluorophenyl)-4,4-dimethyl-4,5-dihydrooxazole (8.9 g, 46 mmol) in 40 mL of THF was heated at 45 °C for 48 h. After hydrolysis, evaporation of THF, and extraction of the aqueous layer with diethyl ether, the solution was dried with $MgSO_4$. After concentration, the residue was purified by chromatography on a silica gel column with hexane/ether (95:5) as the eluent. Yield: 70% (9.2 g). ^{31}P NMR ($CDCl_3$): δ = 0.2. ^1H NMR ($CDCl_3$): δ = 1.43 [s, 6 H, $C(CH_3)_2$], 2.09 (dd, $^4J_{P,H}$ = 4.0, ^4J = 0.5 Hz, 6 H, CH_3), 4.13 (s, 2 H, OCH_2), 6.59 (dd, $J_{P,H}$ = 34.6, ^4J = 0.5 Hz, 2 H, P−CH), 7.2−7.3 (m, 3 H, Ar-H), 7.7−7.8 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 17.7 (d, ^3J = 2.8 Hz, CH_3), 28.5 [$C(\mathit{C}H_3)_2$], 68.4 [$\mathit{C}(CH_3)_2$], 79.0 (OCH_2), 127.7 (CH-Ar), 128.9 (P−CH), 129.1 (d, ^2J = 4.3 Hz, C), 130.3 (CH-Ar), 131.2 (d, ^2J = 19.6 Hz, C), 133.4 (CH-Ar), 135.1 (d, ^1J = 21.4 Hz, C), 147.9 (d, ^2J = 10.6 Hz), 161.8 (s, C=N).

{1-(2-Isopropyl-5-methylcyclohexyl)-3,4-dimethylphosphole}W-(CO)$_5$ (4a): A solution of hexacarbonyltungsten (1.55 g, 4.4 mmol) in 250 mL of THF was irradiated under UV light for 30 min. To this solution was added a solution of **3a** (1.0 g, 4 mmol) in 10 mL of THF. After 1 h of stirring, the solvent was evaporated. The product was then purified by chromatography on silica gel, with hexane as eluent (R_f = 0.25), affording **4a** as a yellow powder. Yield: 91% (2.1 g). ^{31}P NMR ($CDCl_3$): δ = 11.4 ($^1J_{P,W}$ = 203.2 Hz). ^1H NMR ($CDCl_3$): δ = 0.80 (d, ^3J = 6.0 Hz, 3 H, Me), 0.92 (d, ^3J = 6.0, Hz, 3 H, Me), 0.93 (d, ^3J = 6.1 Hz, 3 H, Me), 1.14−1.80 (m, 8 H), 2.15 (s, 6 H, CH_3), 2.32−2.45 (m, 1 H), 2.77 (s, 1 H), 6.43 (d, $^2J_{P,H}$ = 37.2 Hz, 1 H, PCH), 6.53 (d, $^2J_{P,H}$ = 36.7 Hz, 1 H, PCH). ^{13}C NMR ($CDCl_3$): δ = 17.8 (d, ^3J = 3.4 Hz, Me), 17.1 (d, ^3J = 4.4 Hz, Me), 21.6 (Me), 21.8 (Me), 22.24 (Me), 26.0 (d, J = 2.8 Hz, CH_2), 28.8 (CH), 30.13 (CH), 35.4 (CH_2), 39.8 (d, J = 5.9 Hz, CH_2), 42.1 (d, J = 14.6 Hz, CH), 50.9 (d, J = 6.0 Hz, CH), 131.3 (d, ^1J = 38.1 Hz, PCH), 131.8 (d, ^1J = 35.2 Hz, PCH), 146.3 (d, ^2J = 9.3 Hz, C), 146.5 (d, ^2J = 9.0 Hz, C), 197.0 (d, ^2J = 6.2 Hz, 4 CO_{cis}), 199.3 (d, ^2J = 16.8 Hz, CO_{trans}). MS (EI): m/z (%) = 574 (7) [M^+], 192 (100).

{1-[(6,6-Dimethylbicyclo[3.1.1]hept-2-yl)methyl]-3,4-dimethyl-1*H*-phosphole}W(CO)$_5$ (4b): A mixture of lithium 3,4-dimethylphospholide (56 mmol), prepared from lithium metal and 3,4-dimethyl-1-phenylphosphole (10.5 g, 56 mmol) in 60 mL of THF, and hexacarbonyltungsten (19.7 g, 56 mmol) was stirred for 24 h at room temperature. Then 13.0 g (56 mmol) of myrtanyl mesylate were added and the mixture was stirred again for 48 h. After hydrolysis, the THF was evaporated under vacuum. The residue was extracted with diethyl ether, and the organic layer dried with $MgSO_4$. The product was then purified by chromatography on silica gel with hexane as eluent. Yield: 42% (13.5 g). ^{31}P NMR ($CDCl_3$): δ = 5.8 ($J_{P,W}$ = 206.9 Hz). ^1H NMR ($CDCl_3$): δ = 0.85 (d, J = 12.3 Hz, 1 H), 0.94 [s, 3 H, $C(CH_3)_2$], 1.19 [s, 3 H, $C(CH_3)_2$], 1.2−1.4 (m, 1 H), 1.8−2.1 (m, 8 H), 2.16 (s, 6 H, CH_3), 2.2−2.3 (m, 1 H), 6.28 (d, $^2J_{P,H}$ = 36.7 Hz, 1 H, P-CH), 6.33 (d, $^2J_{P,H}$ = 36.7 Hz, 1 H, P−CH). ^{13}C NMR ($CDCl_3$): δ = 17.1 (Me), 17.3 (Me), 23.3 (CH_3), 23.9 (d, ^3J = 4.7 Hz, CH_2), 26.1 (CH_2), 27.8 (CH_3), 32.9 (CH_2), 38.4 ($P-CH_2-\mathit{C}H$), 38.5 [$\mathit{C}(CH_3)_2$], 38.7 (d, ^1J = 22.9 Hz, $P-CH_2$), 40.8 (CH), 48.1 (d, ^3J = 10.3 Hz, CH), 129.3 (d, ^1J = 17.0 Hz, P−CH), 130.1 (d, ^1J = 18.1 Hz, P−CH), 149.8 (d, ^2J = 7.8 Hz, C), 150.2 (d, ^2J = 7.8 Hz, C), 196.4 (d, ^2J = 7.2 Hz, 4 CO_{cis}), 199.3 (d, ^2J = 16.7 Hz, CO_{trans}). MS: m/z (%) = 572 (26) [M^+], 407 (100). $C_{21}H_{25}O_5PW$ (572.23): calcd. C 44.08, H 4.40; found C 43.69, H 4.41.

{(*S*)-2-[2-(3,4-Dimethyl-1*H*-phosphol-1-yl)phenyl]-4-isopropyl-4,5-dihydro-1,3-oxazole}W(CO)$_5$ (4c): A solution of hexacarbonyltungsten (0.89 g, 2.5 mmol) in 250 mL of THF was irradiated under UV for 30 min. To this solution was added a solution of **3c** (0.76 g, 2.5 mmol) in 10 mL of THF. After 30 min of stirring, the solvent was evaporated. The product was then purified by chromatography on silica gel with a hexane/diethyl ether gradient (from 24:1 to 9:1) affording **4c** as a yellow powder (R_f = 0.4 in hexane/diethyl ether, 3:2),. Yield: 85% (1.34 g). ^{31}P NMR ($CDCl_3$): δ = 9.2 ($^1J_{P,W}$ = 213 Hz). ^1H NMR ($CDCl_3$): δ = 1.00 [d, J = 6.7 Hz, 3 H, $CH(C\mathit{H}_3)_2$], 1.09 [d, J = 6.7 Hz, 3 H, $CH(C\mathit{H}_3)_2$], 2.08 [m, J = 5.3 Hz, 1 H, $C\mathit{H}(CH_3)_2$], 2.12 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 4.22−4.53 (m, 3 H, CHN and OCH_2), 6.64 (d, $J_{P,H}$ = 33.0 Hz, 1 H, P−CH), 6.90 (d, $J_{P,H}$ = 32.9 Hz, 1 H, P−CH), 7.39−7.45 (m, 2 H, Ar-H), 7.57−7.67 (m, 1 H, Ar-H), 8.0−8.1 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 17.1 (d, ^3J = 10.1, Me), 17.3 (d, ^3J = 11.1 Hz, Me), 17.6 [$CH(\mathit{C}H_3)_2$], 19.0 [$CH(\mathit{C}H_3)_2$], 32.3 [$\mathit{C}H(CH_3)_2$], 69.6 (OCH_2), 72.7 (CHN), 129.1 (d, J = 10.5 Hz), 129.6, 129.7, 130.0 (d, J = 6.0 Hz), 130.6, 130.7, 131.8 (d, J = 7.0 Hz), 134.0 (d, ^1J = 35.1 Hz, PCH), 148.9 (d, ^2J = 9.8 Hz, C), 149.1 (d, ^2J = 10.2 Hz, C), 162.1 (C=N), 196.9 (d, ^2J = 7.1 Hz, 4 CO_{cis}), 200.0 (d, ^2J = 18.5 Hz, CO_{trans}). MS: m/z (%) = 623 (1) [M^+], 595 (33) [M − CO], 380 (100).

{2-[2-(3,4-Dimethyl-1*H*-phospholyl)phenyl]-4,4-dimethyl-4,5-dihydro-1,3-oxazole}W(CO)$_5$ (4d): A solution of hexacarbonyltungsten (1.85 g, 5.2 mmol) in 250 mL of THF was irradiated under UV light for 30 min. To this solution was added a solution of **3d** (1.5 g, 5.2 mmol) in 10 mL of THF. After 30 min of stirring, the solvent was evaporated. The product was then purified by chromatography on silica gel, with a hexane/diethyl ether gradient. Complex **4c** was obtained as a yellow powder (R_f = 0.35 in hexane/diethyl ether, 3:2). Yield: 80% (2.54 g). ^{31}P NMR ($CDCl_3$): δ = 11.8 ($^1J_{P,W}$ = 214 Hz). ^1H NMR ($CDCl_3$): δ = 1.50 [s, 6 H, $C(CH_3)_2$], 2.12 (s, 6 H, CH_3), 4.19 (s, 2 H, OCH_2), 6.72 (dd, $J_{P,H}$ = 33.2, ^4J = 0.8 Hz, 2 H, P−CH), 7.37−7.47 (m, 2 H, Ar-H), 7.53−7.63 (m, 1 H, Ar-H), 7.98−8.04 (m, 1 H, Ar-H). ^{13}C NMR ($CDCl_3$): δ = 17.3 (d, ^3J = 11.8 Hz, CH_3), 28.3 [$C(\mathit{C}H_3)_2$], 68.8 [$\mathit{C}(CH_3)_2$], 79.2 (OCH_2),129.3 (d, J = 5.1 Hz, C), 128.8, 129.4, 129.7, 130.5, 130.7, 130.8, 131.9, 132.0, 134.1 (d, ^1J = 35.1 Hz, PCH), 149.1 (d, ^2J = 10.7 Hz, C), 160.9 (C=N), 197.2 (d, ^2J = 7.2 Hz, CO_{cis}), 200.4 (d, ^2J = 19.6 Hz, CO_{trans}).

{Dimethyl 7-[(6,6-dimethylbicyclo[3.1.1]hept-2-yl)methyl]-5,6-dimethyl-7-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate}W(CO)$_5$ (5b): To a solution of **4b** (11.4 g, 20 mmol) in 50 mL of toluene was added 15 mL (120 mmol) of dimethyl acetylenedicarboxylate. The solution was heated to 84 °C for 30 h. The solvent was evaporated under vacuum. The residue was purified by chromatography on silica gel with hexane/diethyl ether (95:5) as the eluent. Recrystallization afforded pure **5b** as yellow crystals. Yield: 74% (10.5 g). ^{31}P NMR ($CDCl_3$): δ = 217.5 ($^1J_{P,W}$ = 234.3 Hz). ^1H NMR ($CDCl_3$): δ = 0.90 (d, J = 9.9 Hz, 1 H) 0.97 [s, 3 H, $C(CH_3)_2$], 1.16 [s, 3 H, $C(CH_3)_2$], 1.40 (m, 1 H), 1.72−1.80 (m, 1 H), 1.83−1.90 (m, 3 H), 1.94 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 2.19−2.58 (m, 5 H), 3.56 (m, $^2J_{P,H}$ = 3.0, ^4J = 3.0 Hz, 2 H, P−CH), 3.82 (s, 3 H, OCH_3), 3.84 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ = 15.9 (Me), 16.0 (Me), 22.6 (d, ^3J = 4.5 Hz, CH_2), 22.6 (CH_3), 26.2 (CH_2), 27.9 (CH_3), 33.8 (CH_2), 38.3 (d, ^1J = 17.9 Hz, $P-CH_2$), 38.5 [$\mathit{C}(CH_3)_2$], 41.0 (CH), 43.1 ($P-CH_2\mathit{C}H$), 47.3 (d, ^3J = 7.7 Hz, CH), 52.5 (OMe), 59.9 (d, ^1J = 19.6 Hz, P-CH), 60.3 (d, ^1J = 18.4 Hz, P-CH), 138.9 (d, ^2J = 2.6 Hz, C), 139.1 (d, ^2J = 14.6 Hz, C), 145.3 [d, ^2J = 5.1 Hz, $\mathit{C}(CO_2Me)$], 146.0 [d, ^2J = 4.8 Hz, $\mathit{C}(CO_2Me)$], 165.0 [d, ^3J = 3.0 Hz, $C(\mathit{C}O_2Me)$], 165.4 [d, ^3J = 2.7 Hz, $C(\mathit{C}O_2Me)$], 196.2 (d, ^2J = 6.6 Hz, 4 CO_{cis}), 197.8 (d, ^2J = 25.7 Hz, CO_{trans}). MS: m/z (%) = 714 (4) [M^+], 191 (100).

(7-Aza-1-phosphabicyclo[2.2.1]hept-2-ene)W(CO)$_5$ Complexes 9a and 9b: A solution of **4c** (0.66 g; 1.0 mmol) and dimethyl acetylenedicarboxylate (0.26 mL; 2.1 mmol) in 3 mL of toluene was heated under reflux for 15 h. The crude mixture was purified directly by chromatography on silica gel with toluene as eluent. Two diastereomers were obtained in a 4:1 ratio. Yield: 63% (0.43 g). ^{31}P NMR (toluene): δ = 38.5 (minor diastereomer), 41.8 (major diastereomer). The mixture was dissolved in toluene and layered with hexane. Storage of the solution at 6 °C gave orange crystals of the main diastereomer. ^{31}P NMR (CDCl$_3$): δ = 42.1 ($^1J_{P,W}$ = 289 Hz). ^{1}H NMR (CDCl$_3$): δ = 0.68 [d, J = 7.0 Hz, 3 H, CH(CH_3)$_2$], 0.71 [d, J = 6.6 Hz, 3 H, CH(CH_3)$_2$], 2.00 [m, J = 3.5 Hz, 1 H, CH(CH$_3$)$_2$], 3.33 (m, J = 14.9 et 3.5 Hz, 1 H, CHN), 3.54 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 4.00 (AB, J = 7.7 Hz, 2 H, OCH$_2$), 6.91−7.14 (m, 2 H, Ar-H), 7.33−7.38 (m, 1 H, Ar-H), 7.41−7.53 (m, 1 H, Ar-H). ^{13}C NMR (CDCl$_3$): δ = 14.5 (Me), 19.8 (Me), 29.0 [CH(CH$_3$)$_2$], 52.6 (OMe), 52.7 (OMe), 58.6 (d, ^2J = 2.6 Hz, N−CH), 72.9 (d, ^3J = 7.6 Hz, OCH$_2$), 115.8 (N−C−O), 121.3 (d, J = 3.0 Hz, CH-Ar), 126.4 (d, J = 12.3 Hz, CH-Ar), 128.5 (d, J = 15.6 Hz, CH-Ar), 129.5 (CH-Ar), 142.6 (C-Ar), 146.4 [P−C=C(CO$_2$Me)], 148.8 [d, ^1J = 44.2 Hz, P−C(CO$_2$Me)], 160.4 (d, J = 6.8 Hz, P−C-Ar), 164.0 [d, ^2J = 14.3 Hz, P−C(CO$_2$Me)], 164.2 [d, J = 12.1 Hz, P−C=C(CO$_2$Me)], 194.2 (d, ^2J = 8.1 Hz, W−CO$_{cis}$), 195.9 (d, ^2J = 30.3 Hz, W−CO$_{trans}$).

(7-Aza-1-phosphabicyclo[2.2.1]hept-2-ene)W(CO)$_5$ (9d): A solution of **4d** (2.0 g; 3.3 mmol) and dimethyl acetylenedicarboxylate (0.9 mL; 7.3 mmol) in 8 mL of toluene was heated under reflux for 14 h. The crude mixture was purified directly by chromatography on silica gel with toluene as eluent. The product was dissolved in toluene and layered with hexane. Storage of the solution at 6 °C gave **9d** as orange crystals. Yield: 54% (1.2 g). ^{31}P NMR (CDCl$_3$): δ = 32.2 ($^1J_{P,W}$ = 286 Hz). ^{1}H NMR (CDCl$_3$): δ = 1.16 [s, 3 H, C(CH$_3$)$_2$], 1.24 [s, 3 H, C(CH$_3$)$_2$], 3.53 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.98 (AB, 2 H, OCH$_2$), 6.92−7.14 (m, 2 H, Ar-H), 7.34−7.44 (m, 2 H, Ar-H). ^{13}C NMR (CDCl$_3$): δ = 25.8 [d, J = 6.3 Hz, C(CH$_3$)$_2$], 28.3 [C(CH$_3$)$_2$], 52.4 (OMe), 52.7 (OMe), 60.1 [C(CH$_3$)$_2$], 85.9 (d, ^3J = 4.7 Hz, OCH$_2$), 115.0 (s, N−C), 121.0 (d, J = 3.8 Hz, CH-Ar), 126.1 (d, J = 12.2 Hz, CH-Ar), 127.7 (d, J = 15.6 Hz, CH-Ar), 128.95 (CH-Ar), 145.2 (C-Ar), 149.2 [d, J = 5.9 Hz, P−C=C(CO$_2$Me)], 149.3 [d, J = 43.8 Hz, P−C(CO$_2$Me)], 160.9 (d, J = 5.9 Hz, P−C(Ar)], 163.4 [d, J = 14.0 Hz, P−C(CO$_2$Me)], 164.1 [d, J = 11.2 Hz, P−C=C(CO$_2$Me)], 194.4 (d, J = 8.1 Hz, W−CO$_{cis}$), 195.9 (d, J = 30.2 Hz, W−CO$_{trans}$). $C_{22}H_{18}NO_{10}PW$ (671.19): calcd. C 39.37, H 2.70; found C 39.33, H 2.67.

2-{2-[(*S*)-4-Isopropyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-3,4-dimethyl-1-phosphaferrocene (11a and 11b): A solution of **3c** (0.73 g, 2.4 mmol) and dicarbonyl(η^5-cyclopentadienyl)iron dimer (0.42 g, 1.2 mmol) in 40 mL of toluene was heated at 160 °C for 4 h under 8 bar of CO. The carbon monoxide pressure was then released and the solution heated for additional 3 h. The solution was then allowed to cool to room temperature. The final products **11a** and **11b** were characterized only by ^{31}P NMR as the crude mixture. Two diastereomers were present in a 2:1 ratio. ^{31}P NMR (toluene): δ = −67.1 (minor diastereomer), −68.0 (major diastereomer).

(μ-{2-{2-[(*S*)-4-Isopropyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-3,4-dimethyl-1-phosphaferrocene})[W(CO)$_5$]$_2$ (12a and 12b): A solution of W(CO)$_5$(THF), prepared from 1.70 g (4.8 mmol) of hexacarbonyltungsten in 250 mL of THF, was poured into the crude mixture of **11a**,**b**. The solution was stirred at room temperature for 0.5 h. After evaporation of the solvent, the mixture was purified by chromatography on silica gel with toluene, affording **12a** and **12b** as an orange powder. The chelate compounds **13a** and **13b** were also isolated from the reaction mixture. Yield of **12a**,**b** from **3c** was 60% (1.53 g). The major diastereomer [(*S*,*S*)-**12a**] was obtained in pure form after crystallization from hexane. **12a**: ^{31}P NMR (CDCl$_3$): δ = −34.5 ($^1J_{P,W}$ = 263, $^2J_{P,H}$ = 32.4 Hz). ^{1}H NMR (CDCl$_3$): δ = 0.42 [d, J = 6.7 Hz, 3 H, CH(CH_3)$_2$], 0.88 [d, J = 7.0 Hz, 3 H, CH(CH_3)$_2$], 2.11 (s, 3 H, CH$_3$), 2.20 (s, 3 H, CH$_3$), 2.63 [m, 1 H, CH(CH$_3$)$_2$], 3.70 (d, $J_{P,H}$ = 32.4 Hz, P−CH), 3.93−4.34 (m, 3 H, CHN, OCH$_2$), 4.51 (s, 5 H, Cp), 7.49−7.61 (m, 4 H, Ar-H). ^{13}C NMR (CDCl$_3$): δ = 12.9 [CH(CH$_3$)$_2$], 15.4 (d, J = 3.0 Hz, Me), 16.2 (d, J = 4.5 Hz, Me), 19.0 [CH(CH$_3$)$_2$], 29.9 [CH(CH$_3$)$_2$], 67.8 (OCH$_2$), 69.9 (P−CH), 74.1 (Cp), 77.5 (CHN), 93.1 (C), 93.12 (C), 93.7 (d, J = 2.2 Hz, P−C), 127.7 (CH-Ar), 130.1 (CH-Ar), 130.9 (d, J = 3.2 Hz, C), 131.3 (CH-Ar), 133.9 (d, J = 3.5 Hz, CH-Ar), 134.4 (d, J = 13.8 Hz, C-2′), 171.6 (C=N), 194.5 (d, J = 8.0 Hz, CO$_{cis\text{-}P}$), 197.8 (CO$_{cis\text{-}N}$), 197.8 (d, J = 32.0 Hz, CO$_{trans\text{-}P}$), 200.8 (CO$_{trans\text{-}N}$). $C_{33}H_{26}FeNO_{11}PW_2$ (1067.06): calcd. C 37.14, H 2.46; found C 37.22, H 2.33. [α]$_D$ = −249 (c = 1, toluene). The structure of **12a** has been confirmed by X-ray diffraction studies. The minor diastereomer (*R*,*S*)-**12b** was characterized only by ^{31}P NMR (CDCl$_3$): δ = −31.4 ($^1J_{P,W}$ = 261.6, $^2J_{P,H}$ = 31.8 Hz).

(2-{2-[(*S*)-4-Isopropyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-3,4-dimethyl-1-phosphaferrocene)W(CO)$_4$ (13a and 13b): These compounds were obtained as side products during the synthesis of **12a**,**b** and were isolated by chromatography on silica gel. Crystals of the major diastereomer (**13b**) were obtained from a hexane solution. Yield (**13a** and **13b**): 3% (50 mg). ^{31}P NMR (toluene): δ = −0.7 (main diastereomer), −9.6 (minor diastereomer). The structure of **13b** was established by X-ray diffraction studies.

(2-{2-[(*S*)-4-Isopropyl-4,5-dihydro-1,3-oxazol-2-yl]phenyl}-3,4-dimethyl-1-phosphaferrocene)Mo(CO)$_4$ (14a and 14b): To a crude solution of **11a**,**b**, prepared from 2 g (6.7 mmol) of **3c**, was added 1 equiv. of the (MeCN)Mo(CO)$_5$ complex [prepared from 1.76 g (6.7 mmol) of hexacarbonylmolybdenum and 0.74 g (6.7 mmol) of trimethylamine *N*-oxide in 30 mL of acetonitrile]. The solution was stirred at room temperature for 1 h. After evaporation of the solvent, the mixture was purified by chromatography on silica gel with hexane/toluene (4:1), affording an isomeric mixture of the chelate complexes **14a** and **14b** as an orange powder. Yield over two steps: 47% (1.96 g). The minor diastereomer was characterized by ^{31}P NMR (CDCl$_3$): δ = 8.6. The major diastereomer [(*R*,*S*)-**14a**] was obtained in pure form by crystallization in hexane. **(*R*,*S*)-14a:** ^{31}P NMR (CDCl$_3$): δ = 1.5. ^{1}H NMR (CDCl$_3$): δ = 0.86 [d, J = 6.7 Hz, 3 H, CH(CH_3)$_2$], 0.93 [d, J = 7.0 Hz, 3 H, CH(CH_3)$_2$], 2.27 (s, 6 H, CH$_3$), 2.80 [m, 1 H, CH(CH$_3$)$_2$], 3.71 (d, $J_{P,H}$ = 34.0 Hz, P−CH), 4.05−4.20 (m, 3 H, CHN, OCH$_2$), 4.34 (s, 5 H, Cp), 7.11−7.45 (m, 4 H, Ar-H). ^{13}C NMR (CDCl$_3$): δ = 13.5 [CH(CH$_3$)$_2$], 13.9 (Me), 16.9 (d, J = 2.8 Hz, Me), 18.9 [CH(CH$_3$)$_2$], 29.4 [CH(CH$_3$)$_2$], 67.4 (OCH$_2$), 68.8 (d, J = 17.5 Hz, P−CH), 74.5 (Cp), 76.4 (CHN), 90.0 (d, J = 13.1 Hz, P−C), 92.4 (C), 94.1 (d, J = 2.6 Hz, C), 126.4 (CH-Ar), 128.4 (CH-Ar), 129.9 (CH-Ar), 130.1 (d, J = 16.0 Hz), 133.1 (d, J = 5.4 Hz, CH-Ar), 136.9 (d, J = 13.4 Hz, C), 169.5 (C=N), 204.9 (d, J = 12.1 Hz, CO$_{cis\text{-}P}$), 208.4 (d, J = 10.5 Hz, CO$_{cis\text{-}P}$), 215.7 (d, J = 47.0 Hz, CO$_{trans\text{-}P}$), 219.8 (d, J = 9.2 Hz, CO$_{cis\text{-}P}$). IR (ν_{CO}): $\tilde{\nu}$ = 2017 (m), 1895 (s), 1846 cm^{-1} (s). $C_{27}H_{26}FeMoNO_5P$ (627.26): calcd. C 51.70, H 4.18; found C 51.87, H 4.05.

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