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Diastereoselective Cobalt-Mediated [2 + 2 + 2] Cycloadditions of Substituted Linear Enediynes Phosphine Oxides: Scope and Limitations

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Received July 18, 2002

Variously substituted linear enediynes phosphines oxides possessing the double bond at either the terminal or internal position and with the phosphine oxide appended onto the alkyne or the alkene terminus have been prepared. Their cobalt(I)-mediated cyclizations produce the η^4-complexed tricyclic compounds in high yields. The endo/exo selectivity depends on both the position of the phosphine oxide on the enediyne and the position of the double bond in the tether. With chiral phosphine oxides, a certain degree of induction was observed, and depending on the substituents on the phosphorus atom, the diastereoselectivity can reach 74%. Up to now, it is the highest level reported for such a cyclization in which a stereogenic center is created. Regarding all of our results, two reaction pathways involving an initial coordination of the cobalt moiety on the chelating site of the substituent have been suggested to explain the observed selectivities.

Introduction

The [2 + 2 + 2] cycloaddition reaction of three unsaturated partners is nowadays one of the most powerful synthetic tools for forming several carbon−carbon bonds in a single chemical transformation.[1] Particularly, cobalt(I)-mediated intramolecular cyclizations allow the formation of polycyclic compounds, in a highly regio-, chemo-, and stereoselective fashion, starting from acyclic polyunsaturated precursors. A large range of syntheses of natural and unnatural compounds combined with their biological and/or theoretical interest have been proposed by Vollhardt,[2] ourselves,[3] and others[4] who successfully developed the cyclopentadienylcobalt dicarbonyl, [$CpCo(CO)_2$], catalysis for the cyclotrimerization of alkynes, and the [2 + 2 + 2] cyclization of various polyunsaturated systems.

The ultimate development of this reaction would be its asymmetric version, especially for the selective formation of stereogenic centers in the construction of polycyclic compounds. To our knowledge, there are few examples of asymmetric [2 + 2 + 2] cycloaddition reactions. Vollhardt reported one example of asymmetric [2 + 2 + 2] cyclization promoted by chiral cyclopentadienylcobalt complexes, however, with quite low diastereomeric excesses (16−28%)[5] and also some cyclizations of enediynes possessing a racemic stereogenic center in the tether between both unsaturated moieties.[6] Besides, Mori published the use of $Ni(COD)_2$ and chiral ligands to realize asymmetric [2 + 2 + 2] cyclizations.[7] This cycloaddition involves a facial stereodifferentiation between two enantiotopic groups and the selective formation of a nickelacyclopentadiene, which produces isoindolines and isoquinolines having benzylic chiral centers; the enantiomeric

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10.1021/jo026212r CCC: $25.00 © 2003 American Chemical Society
Published on Web 12/04/2002

excesses reached 73%. Another example concerns the enantioselective synthesis of optically active helicen compounds and also involved a nickel(0)-mediated intramolecular [2 + 2 + 2] cocyclization of triynes in the presence of chiral phosphine ligands.[4a,8]

For several years, we have been concerned in our laboratory with the developments of the cobalt version of this reaction, particularly the finding of new unsaturated partners such as allenes[3b,9] and also the utilization of this cyclization in the synthesis of polycyclic natural products.[3a] Recently, we turned our attention to the asymmetric version of this cyclization based on the use of chiral linear enediynes. Our initial efforts were focused on the identification of the most appropriate substituent and its most judicious position on the polyunsaturated precursors.[10] We showed that the level of diasteroselectivity of the [2 + 2 + 2] cyclization of linear enediynes could be improved over those reported in the literature by introducing substituents such as ester, sulfoxide, or phosphine oxide groups at the terminal positions of either the triple or the double bond of the enediynes. The ester and phosphine oxide groups emerged as the most promising substituents for the asymmetric study in terms of stability of the complexed cycloadducts and yields of the cyclization. However, using chiral esters allowed the level of the induction to remain quite low.[3c] On the contrary, in our first attempts with chiral phosphine oxide groups, we observed, by a proper choice of the substituents on the phosphorus atom, a highly stereoselective induction.[11] Although many syntheses of optically active phosphine oxides have been proposed for their use as chiral ligands in organometallic catalysts, only a few examples of asymmetric induction have been reported with their use as chiral auxiliaries. They were involved in 1,3-dipolar cycloadditions,[12] Diels−Alder[13] and Pauson−Khand[13d] reactions, and conjugate additions.

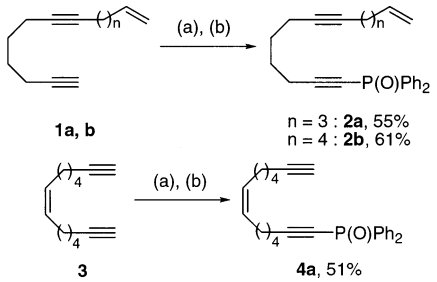
We report herein the full details of the preparation of phosphine oxide-substituted linear enediynes and the scope and limitations of their cyclization, particularly our investigations aimed at the improvement of the stereoselective induction.

Results and Discussion

Various enediynes possessing double bonds at either the terminal or internal position in the chain were prepared. The phosphine oxide substituents were in all cases appended onto the alkyne or the alkene terminus.

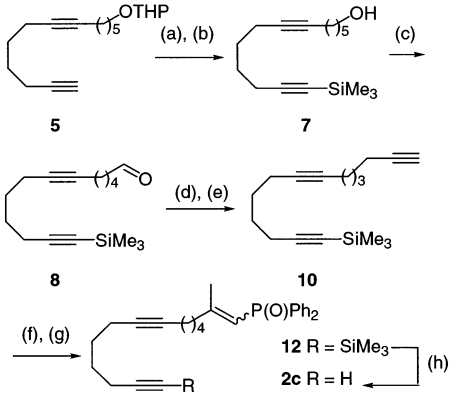
Synthesis of Substituted Enediynes Phosphine Oxides. Enediynes **2a** and **2b** were prepared as outlined in Scheme 1 from the tridec-1-ene-6,12-diyne **1a** and tetradec-1-ene-7,13-diyne **1b**.[2d] Deprotonation of the latter with *n*-BuLi, followed by addition of diphenylphosphinyl chloride, provided **2a** and **2b** in 55 and 61% yields. With the same reaction, tetradec-7-ene-1,13-diyne[3c] **3** led to **4a** in 51% yield.

SCHEME 1. Preparation of Enediynes 2a and 2b[a]



[a] Conditions: (a) *n*-BuLi, −78 °C, THF. (b) $ClP(O)Ph_2$, from −78 °C to room temperature.

SCHEME 2. Preparation of Precursor 2c[a]



[a] Conditions: (a) (i) *n*-BuLi, −78 °C, THF; (ii) Me_3SiCl, from −78 °C to room temperature, yield of **6** = 98%. (b) cat. PTSA, MeOH, **7**: 97%. (c) $(COCl)_2$, DMSO, Et_3N, from −78 °C to room temperature, CH_2Cl_2, yield of **8** = quant. (d) CBr_4, PPh_3, CH_2Cl_2, yield of **9** = 96%. (e) *n*-BuLi, −78 °C, THF, yield of **10** = quant. (f) (i) *n*-BuLi, −78 °C, THF; (ii) $ClP(O)Ph_2$, from −78 °C to room temperature, yield of **11** = 61%. (g) MeMgBr, CuCl, Et_2O, rt, yield of (*Z*)-**12** = 32%, yield of (*E*)-**12** = 48%. (h) KF, DMSO, rt, yield of (*Z*)-**2c** = 95%, yield of (*E*)-**2c** = 99%.

The precursors (*E*)-**2c** and (*Z*)-**2c** were prepared as presented in Scheme 2 from the previously described 2-trideca-6,12-diynyloxy-tetrahydropyran **5**.[3c] The sequence (silylation of the triple bond, cleavage of the THP ether, and Swern oxidation) furnished aldehyde **8** in 95% overall yield. Then, chain extension[14] afforded triyne **10** in 98% yield. After introduction of the diphenylphosphine oxide substituent on the terminal triple bond, the 1,4-addition of methyl Grignard in the presence of cuprous chloride[15] provided **12** in 49% yield as a 3/2 separable mixture of *E*/*Z* stereoisomers. By analogy to the literature,[16] the stereochemistry of the double bond was determined by ^{13}C NMR on the basis of the C−P coupling constants of the vinylic methyl. Other 1,4-addition pro-

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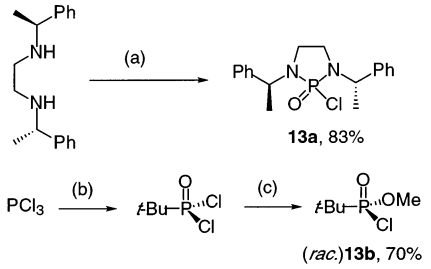
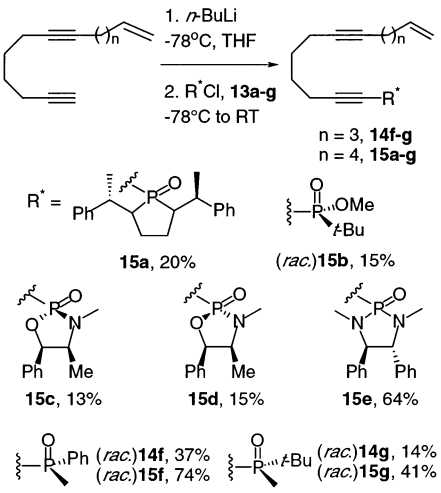
SCHEME 3. Preparation of Phosphines Oxides 13a,b[a]



[a] Conditions: (a) $P(O)Cl_3$, NEt_3, toluene, Δ. (b) (i) *t*-BuCl, $AlCl_3$, CH_2Cl_2; (ii) HCl, H_2O. (c) MeOH, NaH, THF, rt.

SCHEME 4. Preparation of Chiral-Substituted Enediyne Phosphines Oxides 15a−g



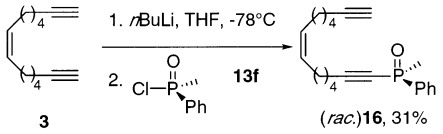
cedures were tried, but the use of both cyanocuprates and $CuBr{\cdot}Me_2S$ failed to deliver the desired products. Finally, desilylation of **12** furnished (*Z*)-**2c** and (*E*)-**2c** in 95 and 99% yields, respectively.

The alkylating chiral phosphine oxide reagents **13a**,**b** were prepared as outlined in Scheme 3. Compound **13a** was obtained in 83% yield from the base-catalyzed condensation of the chiral diamine[17] with phosphorus oxychloride. The sequence (condensation of PCl_3 with *t*-BuCl followed by an acidic aqueous workup[18] and then alkylation of the resulting *tert*-butyldichlorophosphine oxide with sodium methoxide) provided **13b** in 70% overall yield. Finally, the chiral chlorophosphine oxides **13c**−**g** (for their representation, see Scheme 4) were prepared as previously reported in the literature.[19]

The preparation of substituted chiral enediynes phosphine oxides was achieved using the same protocol as above.

Deprotonation of **1a** or **1b** with *n*-BuLi, followed by addition of the chiral chlorophosphine oxide **13a**−**g**, provided the corresponding enediynes **14f**−**g** and **15a**−**g** in yields from 13 to 74% (Scheme 4). It is noteworthy that the formation of **15c** and **15d** results from the alkylation of **1b** with **13d**. In the same manner, the enediyne **3** was alkylated with **13f** giving **16** in 31% yield (Scheme 5).

SCHEME 5. Preparation of Enediyne 16



SCHEME 6. Preparation of the Chiral-Substituted Enediyne Thiophosphine Oxide 15h

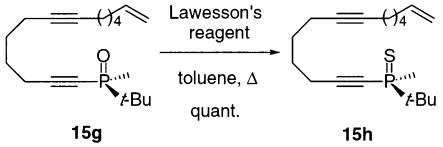
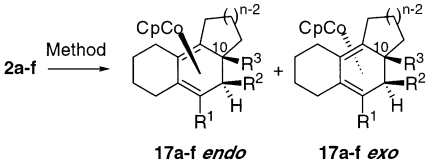


TABLE 1. Cobalt(I)-Mediated Cyclization of Enediynes 2a−f



SM	*n*	method[a]	R^1	R^2	R^3	yield (endo/exo)[e] **17a**−**f**
2a	3	A	$P(O)Ph_2$	H	H	88% (37/63)
2b	4	A	$P(O)Ph_2$	H	H	96% (25/75)
2c[b]	4	B	H	$P(O)Ph_2$	Me	32% (100/0)
2d[c]	3	A	$SiMe_3$	H	H	85% (0/100)
2d[d]		B	$SiMe_3$	H	H	85% (46/54)
2e[d]	4	B	$SiMe_3$	H	H	92% (50/50)
2f[d]	4	B	H	H	H	76% (33/67)

[a] Method A: $CpCo(CO)_2$ (1 equiv), toluene, *hν*, Δ. Method B: $CpCo(CO)_2$ (1 equiv), decane, Δ. [b] (*E*)-**2c**. [c] From ref 3c. [d] From ref 2d. [d] Endo/exo ratio was determined both by ^1H NMR on the basis of the integration of Cp-protons and by ^{31}P NMR.

In addition, the reaction of Lawesson's reagent[20] with **15g** quantitatively provided thiophosphine oxide **15h** (Scheme 6).

Cyclizations of Substituted Enediynes Phosphine Oxides. The cyclizations of the enediynes were conducted using two methods, A and B (Table 1). When the enediyne is substituted at the alkyne terminus, both methods could be used to produce the cycloadducts without affecting the endo/exo ratio. However, method A was usually preferred for better yields and shorter reaction times. Precursors **2a**,**b** afforded red-brown complexes as mixtures of inseparable endo/exo diastereoisomers of **17a**,**b** in very good yields. It is interesting to note that the isolated complexes are highly stable, since they could be purified on silica gel with nondegassed solvents. On the contrary, the behavior of the enediyne substituted at the vinylic position is totally different. Indeed, method B is the only effective procedure and (*E*)-**2c** is the only stereoisomer that reacts under these conditions, furnishing the very unstable cycloadducts **17c** even upon purification on

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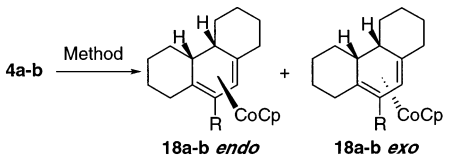
TABLE 2. Cobalt(I)-Mediated Cyclization of Enediynes 4a,b



18a-b *endo* 18a-b *exo*

SM	R	method	yield (endo/exo) **18a**,**b**
4a	$P(O)Ph_2$	A	77% (100/0)
4b[2e]	H	B	63% (0/100)

alumina with degassed solvents. In addition, whatever the procedure used, (*Z*)-**2c** led to intractable materials.

The endo/exo stereochemical assigments of **17a**−**c** relied on spectral interpretations analogous to those of the parent compounds **17d**−**f**. These are based on the characteristic chemical shifts of the angular hydrogen atom 10-H, which is more shielded in the exo diastereomer than in the endo one. Similarly, the ^{13}C resonance at the *endo*-methyne carbon atom C-10 occurs 8−9 ppm downfield from the analogous *exo*-methyne carbon atom.

Several features in these cyclizations are noteworthy, in particular when compared to those reported in the literature.[2d,3c,21] The substitution of the trimethylsilyl group of the enediyne (**2d**) by a phosphine oxide (**2a**) resulted in a slight improvement of the diastereoselectivity (37/63 vs 46/54, while the cyclization of **2d** is totally diastereoselective under thermal conditions). In contrast, the diastereoselectivity of the cyclization of **2b** was really affected, relative to the parent compounds **2e** and **2f**, in favor of the exo complexes. Finally, the cyclization of (*E*)-**2c** is totally diastereoselective in favor of the endo complexes, albeit the yield is quite moderate.

The cyclization of enediyne **4a** was carried out according to method A and led to the very stable cycloadduct **18a** in 77% yield as a unique endo diastereomer as it was also observed for the ester group.[3c] This total diastereoselectivity is completely opposite to that reported for the cyclization of **4b,** which exhibits hydrogen at the alkyne termini[2e] (Table 2).

The endo stereochemical assignment was attributed by ^1H NMR on the basis of the chemical shifts of the angular hydrogens at $\delta = 2.1$ ppm, which are consistent with a cis relationship between those and the cobalt moiety.

To define any degree of chiral induction during the cyclization, we then investigated the behavior of linear enediynes **14f**−**g** and **15a**−**g** bearing chiral phosphine oxides on the alkyne. In all cases, the reactions were performed using method A and the cycloadducts were obtained in high yields with the same endo/exo selectivity as that observed for **2a** (Table 3).

The results from **15a** to **15g** showed that the diastereomeric excess for either the exo diastereomer or the endo one is higher when the stereogenic centers are closer to the triple bond. The best excesses were observed when the phosphorus atom was stereogenic, especially for **15f**, which bears a bulky *tert*-butyl group on phosphorus. The difference of selectivity between **f** and **g** is noticeable either for the formation of the tricyclic 6,6,5- (**19f** vs **19g**) or 6,6,6-compounds (**20f** vs **20g**), the *tert*-butyl group bringing an important sterical discrimination.

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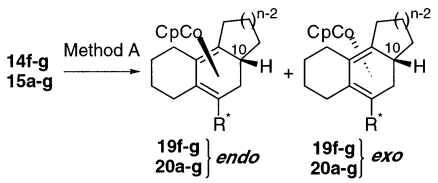
TABLE 3. Cyclizations of Enediynes 14f,g and 15a−g Bearing Chiral Phoshine Oxides

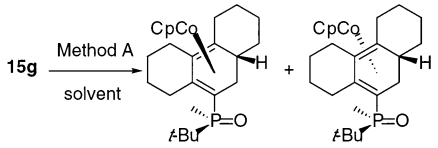


19f-g 20a-g *endo* 19f-g 20a-g *exo*

SM	n	yield (%)	complex	endo (de %)	exo (de %)
14f	3	99	**19f**	35(27)	65(11)
14g	3	93	**19g**	**39(56)**	**61(20)**
15a	4	94	**20a**	24(2)	76(6)
15c	4	83	**20c**	33(24)	67(29)
15d	4	88	**20d**	31(34)	69(36)
15e	4	100	**20e**	22(25)	78(15)
15f	4	80	**20f**	31(42)	69(30)
15g	4	100	**20g**	**29(58)**	**71(60)**[a]

[a] Assigned structure of the major *exo*-**20g** diastereomer was confirmed by X-ray analysis.

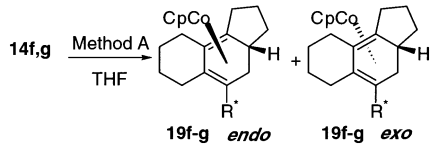
TABLE 4. Influence of Solvent on the Cyclization of 15g



20g *endo* 20g *exo*

solvent	yield (%)	endo (de %)	exo (de %)
toluene	100	29(58)	71(60)
benzene	100	30(64)	70(64)
THF	**97**	**29(72)**	**71(74)**
dioxane	100	28(66)	72(60)
t-butylmethyl ether	74	22(69)	78(70)
cyclohexane	100	23(62)	77(57)
diethyl ether	97	24(58)	76(61)

TABLE 5. Cyclization of 14f and 14g in THF



19f-g *endo* 19f-g *exo*

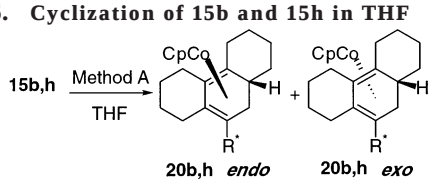
SM	yield (%)	complex	endo (de %)	exo (de %)
14f	100	**19f**	36(30)	64(8)
14g	100	**19g**	**39(58)**	**61(21)**

We also checked the influence of the solvent and ran a series of experiments with **15g** according to procedure A (Table 4). The table shows an increase in the diastereomeric excesses in refluxing THF or *tert*-butylmethyl ether. However, neither the boiling point nor the polarity of the solvent is the determining factor for the improvement of the excesses. Indeed, in ether or dioxane, the excesses are almost the same as in toluene, benzene, or cyclohexane and, in addition, the reaction did not proceed at 0 °C in THF.

Surprisingly, the formation of tricyclic 6,6,5-compounds **19f**,**g** in THF was not accompanied by an increase in the diastereoselectivity related to toluene (Table 5)

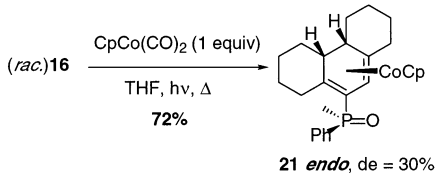
In addition, substitution of the methyl group by a methoxy on the phosphorus atom did not bring any

TABLE 6. Cyclization of 15b and 15h in THF



SM	yield (%)	complex	endo (de %)	exo (de %)
15b	80	**20b**	27(66)	73(68)
15h	29	**20h**	34(58)	66(64)

SCHEME 7. Cyclization of Enediyne 16 in THF



improvement to the diastereoselectivity of the cyclization (Table 6). On the other hand, no increase in the diastereoselectivity has been shown when a sulfur atom replaced the oxygen on phosphorus, as was the case for the [3 + 2] cyclizations.[12b]

Finally, the cyclization of **16** in THF according to method A led to **21** as only one diastereomer (endo), as was observed for **4a**, but the diastereomeric excess remained moderate (30%) (Scheme 7).

According to the literature,[2b,d] two major reaction pathways may be considered to account for the selectivity of the cyclizations. One involves the binding of two alkyne units and leads to a metallacyclopentadiene, which then reacts with the appended alkene via a Diels−Alder reaction to give the cycloadduct. The stereochemistry is set either in the formation of the metallocyclopentadiene (exo complexation) or during the Diels−Alder step (exo transition state). In the second pathway, after the initial formation of a metallacyclopentene, subsequent insertion of the second alkyne furnishes a metallacycloheptadiene that affords by a reductive elimination the cycloadduct. The stereocontrol could occur in these different steps, but it appears more likely to occur during the formation of the metallacyclopentene.

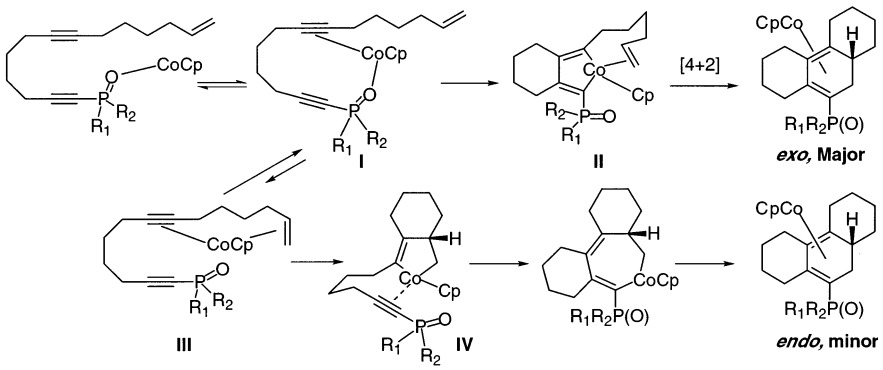
Looking back at the results we obtained, it appears that the position of the phosphine oxide group on the enediyne (acetylenic vs vinylic) could be an additional controlling feature for the endo/exo selectivity. Compared to the group used in the literature ($SiMe_3$, H), the phosphine oxide is a Lewis base. Thus, we suppose that the first step of the cyclization that is responsible for the selectivity could be a Lewis acid/base coordination between the cobalt moiety and the coordinating site of the substituent. Then, when the phosphine oxide is at the alkyne terminus (Scheme 8), the second step could be the complexation of the internal triple bond that is the closest and the electronically richest unsaturation of the tether (**I**). Consequently, to the coordination of both alkynes, the triple bond bearing the substituent is in the coordination sphere of the cobalt, and therefore the oxidative addition leads to the cobaltacyclopentadiene (**II**). The latter could react with the terminal double bond via a [4 + 2] reaction to afford the major exo complexes. However, a second pathway has to be considered: after coordination and a ligand exchange, which could be influenced by the irradiation, the double bond would be complexed to the metal (**III**). Thus, the oxidative coupling could give a cobaltacyclopentene (**IV**). Then, the insertion of the second triple bond into the cobalt−carbon bond followed by a reductive elimination anti to the six-membered ring could afford the minor endo complexes.

This initial coordination could also explain the major endo selectivity observed, when the phosphine oxide is at the alkene terminus, the pathway via the cobaltacyclopentene in that case being major.

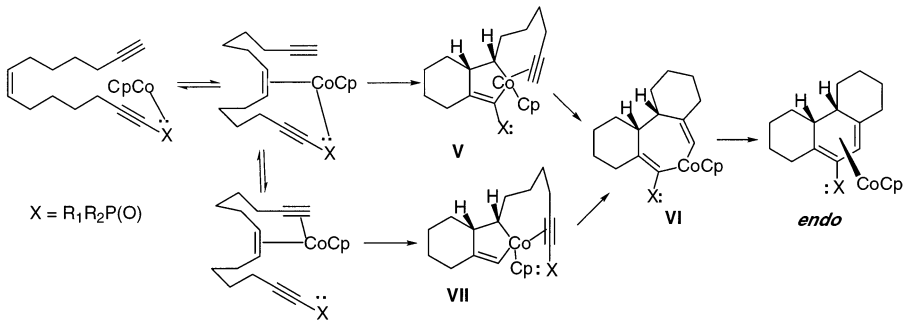
Similarly, these pathways could validate the total endo selectivity observed when the double bond is internal (Scheme 9). Indeed, after the initial coordination, the complexation of the second unsaturation might be expected to be governed by electronic as well as stereoelectronic factors. Therefore, the complexation of the double bond would probably be favored over that of the other triple bond, which would have given a macrocycle. Oxidative addition would give cobaltacyclopentene **V**, which in turn would rearrange to the endo cycloadduct. It is obvious that a ligand exchange and the subsequent steps led to the same cobaltacycloheptadiene **VI** and then to the endo cycloadduct.

To demonstrate the initial coordination we proposed, we ran some additional experiments with **2b** in the presence of a Lewis acid such as $ZnCl_2$. For example, we added 1 equiv of $ZnCl_2$ to precoordinate the phosphine oxide group before adding $CpCo(CO)_2$ and carrying out the reaction. Indeed, the cyclization led to **17b** in 78% yield as a 48:52 mixture of exo/endo cycloadducts. The

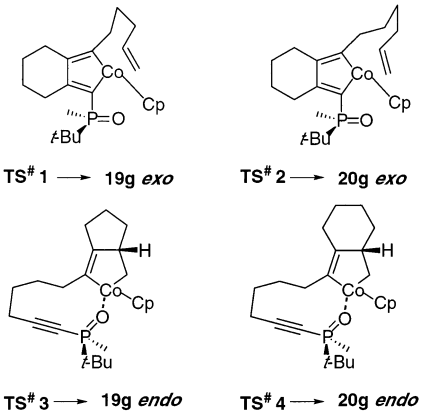
SCHEME 8. Phosphine Oxide at the Alkyne Terminus: Possible Pathways for the Formation of the Endo/Exo Cycloadducts



SCHEME 9



SCHEME 10



loss of selectivity means that the postulated coordination is indeed effective.

The length of the tether does not really influence the endo/exo selectivity, because this ratio is almost identical for the formation of the 6,6,6- and 6,6,5-cycloadducts (in the case of $P(O)Ph_2$, 25/75 vs 37/63). However, with chiral phosphine oxide, the diastereomeric excesses are quite different: for example, the de for exo-**19g** complexes is 21%, whereas it reaches up 74% for exo-**20g**. This difference could be explained by the two transition states of the [4 + 2] reaction, TS-1 and TS-2, leading to the corresponding cycloadducts (Scheme 10).

The most favored approach of the polyunsaturated partners in which the nonbonded interactions and $A_{1,3}$ strains were minimized is the exo approach in which the tether is in an envelop conformation for TS-1 and a chairlike for TS-2. Probably, the chairlike conformation allows a better overlapping of the π orbitals and develops stronger interactions with the chiral auxiliary than the envelop conformation and gives rise to a better facial diastereodifferentiation. For the endo complexes, the difference between the de is not sufficiently significant to invoke an effect of the length of the tether on transition states TS-3 and TS-4.

Conclusion

In summary, the cobalt(I)-mediated cyclization of linear enediynes bearing a phosphine oxide at the acetylenic position provided predominantly exo cycloadducts in high yields. Those cycloadducts as well as the endo ones are very air-stable and can easily be purified and handled. On the opposite, the cyclization was totally diastereoselective in favor of the endo complexes either when the double bond was internal and an acetylenic phosphine oxide was present or when the phosphine oxide is at the terminal vinylic position, but in the latter case, the yield is moderate and the adduct very unstable.

When chiral phosphine oxides were employed, we observed a certain degree of induction during the cyclization. Depending of the substituents on the phosphorus atom, especially if the latter is stereogenic, the diastereoselectivity can reach 74%, and up to now, this level is the highest reported in such a cyclization. In relation with the position of the phosphine oxide on the enediyne, two reaction pathways could be proposed to explain the exo/endo selectivity, an initial coordination between the cobalt moiety and the chelating site of the substituent appearing to be the determining factor for the selectivity. Even if it is impossible to distinguish between these pathways, they are consistent with our results and bring additional information concerning the mechanism of the [2 + 2 + 2] cycloaddition of enediynes.

Experimental Section

Synthesis of Substituted and Chiral Substituted Linear Enediyne Phosphine Oxides. See Supporting Information.

General Procedure for the Cyclization of Enediynes. In most cyclizations, the complexes were obtained as an inseparable mixture of endo/exo cycloadducts (four compounds). In some cases, one couple of cycloadducts is fully described; for the other case, we gave only characteristic data.

Method A. $CpCo(CO)_2$ (0.37 mmol, 1.2 equiv) was added to a boiling solution of the enediyne (0.31 mmol, 1 equiv) in toluene (9 mL), degassed by three freeze−pump−thaw cycles, and irradiated (light from a projector lamp, ELW, 300 W, 80% of its power). The reaction was monitored by TLC, and after completion (about 1 h), the reaction mixture was purified by flash chromatography either on deactivated alumina (4% H_2O) or on silica gel.

Method B. $CpCo(CO)_2$ (0.37 mmol, 1.2 equiv) was added to a boiling solution of the enediyne (0.31 mmol, 1 equiv) in decane (9 mL) and degassed by three freeze−pump−thaw cycles, and the reaction mixture was stirred at reflux overnight. Then, the solution was purified by flash chromatography on deactivated alumina (4% H_2O) or on silica gel.

Complexes 17a. Yield = 88%. Method A. **Exo** (characteristic data): ^{1}H NMR (400 MHz, C_6D_6) δ 4.93 (s, 5H), 3.87 (dt, J = 17.3, 5.6 Hz, 1H), 1.22 (dd, J = 8.2, 2.5 Hz, 1H), 0.69 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 136.3 (J = 99.1 Hz), 136.1 (J = 91.0 Hz), 133.2 (J = 8.1 Hz), 132.0 (2C, J = 10.1 Hz), 131.8 (2C), 130.7 (J = 8.1 Hz), 128.5 (J = 13.2 Hz), 128.3 (J = 10.1 Hz), 127.7 (2C, J = 11.1 Hz), 94.1 (J = 8.1 Hz), 89.1 (J = 12.1 Hz), 83.2 (5C), 76.8, 48.6 (J = 91 Hz), 40.9 (J = 12.1 Hz), 36.4 (J = 10.1 Hz); ^{31}P NMR (162 MHz, C_6D_6) 37.5. **Endo** (characteristic data): ^{1}H NMR (400 MHz, C_6D_6) δ 4.85 (s, 5H), 4.19 (dt, J = 12.7, 4.6 Hz, 1H), 1.19 (dd, J = 8.2, 3.1 Hz, 1H),

0.58−0.47 (m, 1H), −0.43 (dd, J = 11.2, 9.1 Hz); ^{13}C NMR (100 MHz, C_6D_6) δ 136.7 (J = 103.1 Hz), 136.4 (J = 87.0 Hz), 132.5 (2C, J = 8.1 Hz), 132.2 (2C, J = 10.1 Hz), 131.2 (J = 12.1 Hz), 130.4 (2C), 128.5 (J = 13.2 Hz), 128.2 (J = 8.1 Hz), 127.9 (J = 9.1 Hz), 95.0 (J = 4.0 Hz), 88.8 (J = 12.1 Hz), 83.2 (5C), 75.8, 52.6 (J = 8.1 Hz), 32.8 (J = 6.1 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ 37.0. **(Endo + Exo) 17a** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 8.22−8.16 (m, 2H), 8.14−7.96 (m, 4H), 7.92−7.86 (m, 2H), 7.24−7.12 (m, 12H), 2.51−2.21 (m, 4H), 2.20−1.28 (m, 23H), 1.10−0.95 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 36.0, 32.5, 31.0, 30.0, 28.4, 28.3, 27.7, 26.9, 26.8, 24.1, 23.9, 23.5, 23.2 (2C); IR (neat) 3060, 2940, 1480, 1435, 1235 cm^{-1}.

Complexes 17b. Yield = 96%. Method A. **Exo** (characteristic data): ^{1}H NMR (400 MHz, C_6D_6) δ 8.21−8.13 (m, 2H), 8.05−8.00 (m, 1H), 7.95−7.87 (m, 2H), 7.30−7.10 (m, 5H), 4.98 (s, 5H), 3.95 (d, J = 2.6 Hz, 1H), 2.31 (t, J = 5.1 Hz, 1H), 1.86 (m, 1H), 1.53 (m, 1H), 1.00 (t, J = 7.1 Hz), 2.53−0.90 (m, 12H), 0.71 (m, 1H), 0.51 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 142.2 (2C, J = 113.2 Hz), 136.4 (2C, J = 13.9 Hz), 132.6 (2C, J = 9.0 Hz), 131.7 (2C, J = 8.8 Hz), 130.3 (2C), 127.6 (2C, J = 10.3 Hz), 90.8 (J = 12.1 Hz), 83.3 (5C), 73.4, 46.5 (J = 93 Hz), 41.6 (J = 10.1 Hz), 33.6; ^{31}P NMR (162 MHz, C_6D_6) δ 36.1. **Endo** (characteristic data): ^{1}H NMR (400 MHz, C_6D_6) δ 4.83 (s, 5H), 2.17 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 130.1 (2C), 128.2 (2C, J = 12.4 Hz), 95.4 (J = 5.3 Hz), 91.3 (J = 12.1 Hz), 83.8 (5C), 73.1, 48.6 (J = 10.1 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ 36.2. **(Endo + Exo) 17b** (unattributed): ^{13}C NMR (100 MHz, C_6D_6) δ 36.7, 36.5 (2C), 33.8, 33.4, 33.3, 32.8, 30.1, 30.0, 29.7, 28.9, 28.3, 28.1, 27.9, 27.5, 26.9, 26.6, 26.5, 26.4, 23.5, 23.3, 19.1 (2C); IR (neat) 3060, 2940, 2860, 1480, 1435, 1235 cm^{-1}.

Complex *endo*-17c. Yield = 32%. Method B: ^{1}H NMR (400 MHz, C_6D_6) δ 8.26−8.00 (m, 4H), 7.36−7.16 (m, 6H), 4.60 (s, 5H), 2.77 (d, 1H, J = 10.8 Hz), 2.03 (s, 3H), 2.00−0.82 (m, 17H); ^{13}C NMR (100 MHz, C_6D_6) δ 138.0 (2C, J = 88.2 Hz), 131.8 (2C, J = 8.1 Hz), 131.5 (2C, J = 9.1 Hz), 131.0 (2C), 130.6 (2C, J = 9.1 Hz), 128.2 (2C, J = 7.1 Hz), 94.0, 93.7, 92.7, 82.2 (5C), 51.9 (J = 8.8 Hz), 46.7 (J = 73 Hz), 43.4, 41.5, 31.4, 30.6, 27.6, 25.4 (2C), 25.2 (J = 9.1 Hz), 24.1, 23.4; ^{31}P NMR (162 MHz, C_6D_6) δ 28.9.

Complex *endo*-18a. Yield = 77%. Method A: ^{1}H NMR (400 MHz, C_6D_6) δ 8.35−8.30 (m, 2H), 8.23−8.18 (m, 2H), 8.10−8.04 (m, 2H), 7.32−7.12 (m, 4H), 4.78 (s, 5H), 4.37 (d, J = 5.6 Hz, 1H), 3.62 (d, J = 12.7 Hz, 1H), 2.21 (tt, J = 12.0, 3.0 Hz, 1H), 2.01 (td, J = 12.0, 3.0 Hz, 1H), 1.85−1.19 (m, 13H), 1.10−0.95 (m, 1H), 0.83−0.76 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 136.2 (J = 99.1 Hz), 134.2 (J = 101.1 Hz), 132.8 (J = 8.1 Hz), 132.3 (J = 8.1 Hz), 132.0 (J = 8.1 Hz), 131.9 (J = 12.1 Hz), 131.3, 131.2, 128.5 (J = 8.1 Hz), 128.4 (J = 9.1 Hz), 128.3 (J = 11.1 Hz), 127.8 (J = 11.1 Hz), 84.0 (J = 44.5 Hz), 82.3 (5C), 79.1 (J = 12.1 Hz), 77.7 (J = 24.3 Hz), 77.4, 49.2, 46.7, 40.7, 37.9, 34.0, 31.7, 31.3, 28.9, 27.9, 27.8; ^{31}P NMR (162 MHz, C_6D_6) δ 31.0; IR (C_6D_6) 3060, 2920, 1440, 1235 cm^{-1}.

Complexes 19f. Yield = 99%. Method A. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.86 (s, 5H) 1.41 (d, J = 14.8 Hz, 3H), −0.43 (dd, J = 12.2, 9.2 Hz, 1H); (minor) 4.76 (s, 5H), 1.69 (d, J = 12.7 Hz, 3H), −0.54 (dd, J = 11.2, 9.2 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 137.8 (J = 183.4 Hz), 94.5 (J = 4.6 Hz), 89.1 (J = 12.1 Hz), 83.1 (5C), 74.9, 52.5 (J = 9.8 Hz), 50.4 (J = 57.0 Hz), 16.0 (J = 47.8 Hz); (minor) 137.8 (J = 183.4 Hz), 94.4 (J = 5.3 Hz), 88.6 (J = 12.0 Hz), 82.9 (5C), 75.6, 51.8 (J = 9.8 Hz), 50.4 (J = 57.0 Hz), 17.3 (J = 46.5 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 36.0; (minor) 40.2. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.88 (s, 5H), 2.49 (td, J = 17.3, 6.1 Hz, 1H), 1.70 (d, J = 12.7 Hz, 3H); (minor) 4.82 (s, 5H), 1.56 (d, J = 11.7 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 137.7 (J = 178.8 Hz), 93.4 (J = 6.1 Hz), 89.0 (J = 11.4 Hz), 82.7 (5C), 76.7, 50.6 (J = 56.1 Hz), 40.9 (J = 12.1 Hz), 18.5 (J = 48.9 Hz); (minor) 138.2 (J = 171.3 Hz), 92.5 (J = 7.6 Hz), 88.9 (J = 11.4 Hz), 82.8 (5C), 76.8, 50.0 (J = 55 Hz), 40.6 (m, J = 12.1 Hz), 13.9 (J = 45.5 Hz); ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 37.3; (minor) 37.8. **(Endo + Exo) 19f** (unattributed): ^{13}C NMR (100 MHz, C_6D_6) δ 132.2 (J = 8.3 Hz), 131.9, 131.8, 131.6 (J = 9.9 Hz), 131.4 (J = 8.3 Hz), 130.9 (J = 9.1 Hz), 130.8 (2C), 130.7 (J = 8.3 Hz), 130.6 (J = 7.6 Hz), 130.5 (J = 5.3 Hz), 130.3 (J = 4.5 Hz), 130.2 (J = 4.5 Hz), 128.7, 128.3 (J = 10.6 Hz), 128.2 (J = 10.6 Hz), 128.2, 128.1(2C), 127.8, 34.3, 34.2, 34.1, 33.9, 33.8, 33.6, 32.9, 32.7, 32.5, 32.4, 31.1, 31.0, 29.8, 29.7, 27.7, 27.6, 27.5, 27.3, 27.2, 27.1, 27.0, 26.9, 25.6, 25.4, 24.0, 23.7, 23.5, 23.3, 23.2, 23.1, 23.0, 22.9; ^{1}H NMR (400 MHz, C_6D_6) δ 8.08−7.87 (m, 8H), 7.35−7.10 (m, 12H), 4.21−3.87 (m), 3.67 (dq, J = 10.2, 6.6 Hz), 2.61 (m), 2.40−1.19 (m), 1.04−0.82 (m).

Complexes 19g. Yield = 93%. Method A. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.78 (s, 5H), 2.13 (m, 1H), 1.45 (d, J = 23.8 Hz, 3H), 1.21 (d, J = 12.2 Hz, 9H), −0.52 (dd, J = 9.7, 1.6 Hz, 1H); (minor) 4.77 (s, 5H), 2.21 (m, 1H), 1.43 (d, J = 24.4 Hz, 3H), 1.26 (d, J = 10.2 Hz, 9H), −0.65 (ddd, J = 9.7, 4.6, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 92.2 (J = 8.1 Hz), 88.0 (J = 10.1 Hz), 83.3 (5C), 74.4, 51.6 (J = 83.0 Hz), 35.2 (J = 58.6 Hz), 53.1 (J = 8.1 Hz), 26.7 (3C), 13.1 (J = 68.7 Hz); (minor) 94.3 (J = 8.2 Hz), 88.0 (J = 10.1 Hz), 83.2 (5C), 75.0, 51.8 (J = 10.1 Hz), 51.6 (J = 83.0 Hz), 35.2 (J = 58.6 Hz), 26.6 (3C), 13.1 (J = 68.7 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 55.8; (minor) 55.8. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.79 (s, 5H), 1.46 (d, J = 23.9 Hz, 3H), 1.18 (d, J = 13.2 Hz, 9H), 0.71 (m, 1H); (minor) 4.82 (s, 5H), 1.42 (d, J = 24.3 Hz, 3H), 1.27 (d, J = 13.2 Hz, 9H), 0.64 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 95.5 (J = 6.1 Hz), 87.7 (J = 12.1 Hz), 83.6 (5C), 77.0, 52.6 (J = 78.0 Hz), 41.9 (J = 11.1 Hz), 35.4 (J = 68.7 Hz), 27.3 (3C), 12.9 (J = 66.7 Hz); (minor) 96.8 (J = 6.1 Hz), 88.3 (J = 10.1 Hz), 83.4 (5C), 76.6, 52.6 (J = 78.0 Hz), 40.4 (J = 10.1 Hz), 35.4 (J = 68.7 Hz), 27.3 (3C), 12.9 (J = 66.7 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 57.4; (minor) 57.4. **(Endo + Exo) 19g** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 4.03 (m, 1H), 2.10−2.60 (m), 1.53−2.08 (m), 0.95−1.15 (m), 0.5−0.78 (m); ^{13}C NMR (100 MHz, C_6D_6) δ 36.0, 35.5, 34.6, 34.3, 34.2, 33.4, 33.3 (3C), 32.8, 32.5 (2C), 31.2, 30.2, 30.0, 29.8, 29.1, 28.5, 28.2, 28.0, 27.9, 27.7, 27.4, 27.1, 24.0, 23.9 (2C), 23.4, 23.2 (2C), 22.7, 22.6; IR (C_6D_6) 2920, 2850, 1440, 1360, 1285, 1140 cm^{-1}.

Complexes 20a. Yield = 94%. Method A. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.68 (s, 5H); (minor) 4.70 (s, 5H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 143.3 (2C), 96.4 (J = 6.1 Hz), 92.0 (J = 16.2 Hz), 72.4, 51.3 (J = 170 Hz), 83.5 (5C), 49.8 (J = 4.1 Hz); (minor) 142.7 (2C), 96.4 (J = 6.1 Hz), 92.0 (J = 16.2 Hz), 83.6 (5C), 72.4, 51.3 (J = 170 Hz), 49.8 (J = 4.1 Hz). ^{31}P NMR (162 MHz C_6D_6) δ: (major) 42.2; (minor) 41.8. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.82 (s, 5H); (minor) 4.81 (s, 5H). ^{13}C NMR (100 MHz C_6D_6) δ: (major) 144.0 (2C), 95.6 (J = 8.1 Hz), 90.4 (J = 14.2 Hz), 83.0 (5C), 72.4, 50.6 (J = 115 Hz), 40.4 (J = 7.1 Hz); (minor) 144.1 (2C), 95.5 (J = 6.1 Hz), 90.4 (J = 14.2 Hz), 82.9 (5C), 72.4, 50.6 (J = 115 Hz), 40.4 (J = 7.1 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 42.9; (minor) 42.8. **(Endo + Exo) 20a** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 8.00−7.15 (m, 40H), 5.48−5.19 (2m), 4.41−4.26 (m), 2.78−2.32 (m), 1.64 (d, J = 7.1 Hz, 3H), 1.28 (d, J = 7.0 Hz, 3H), 2.21−0.5 (m); ^{13}C NMR (100 MHz, C_6D_6) δ 126.7−128.69 (m, 40C), 50.3−53.5 (m, 8C), 36.9, 36.8 (2C), 36.7 (2C), 35.4, 35.3, 35.2, 35.1, 34.0, 33.9, 33.8, 33.3, 33.0, 32.8, 32.7 (2C), 29.7 (2C), 29.4 (2C), 28.9, 28.8, 27.5, 27.4, 27.3, 27.2, 27.1, 27.0 (2C), 26.9 (2C), 26.8, 26.7 (2C), 26.6, 26.5, 24.1, 24.0 (2C), 23.9 (2C), 23.8, 23.7, 16.7−17.9 (m, 8C).

Complexes 20b. Yield = 80%. Method A. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.86 (s, 5H), 3.75 (d, J = 9.6 Hz, 3H), 2.56 (ddd, J = 16.3, 12.2, 5.1 Hz, 1H), 1.30 (d, J = 7.2 Hz, 9H), 0.52 (td, J = 12.2, 3.6 Hz, 1H), −0.05 (ddd, J = 12.2, 7.1, 1.6 Hz, 1H); (minor) 4.81 (s, 5H), −0.08 (ddd, J = 12.4, 6.9, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 83.3 (5C), 48.5 (J = 8.1 Hz), 33.8 (J = 8.1 Hz), 27.0; no characteristic data for the minor endo compound. ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 60.6; (minor)

66.2. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.99 (s, 5H), 3.73 (d, J = 9.6 Hz, 3H), 3.96−3.87 (m, 1H), 2.47 (ddd, J = 15.8, 11.7, 4.6 Hz, 1H), 1.29 (d, J = 9.6 Hz, 9H), 0.74 (t, J = 9.6 Hz, 1H), 0.61 (ddd, J = 13.2, 8.1, 2.0 Hz, 1H); (minor) 4.92 (s, 5H), 3.64 (d, J = 9.5 Hz, 3H), 1.31 (d, J = 9.4 Hz, 9H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 96.2 (J = 10.1 Hz), 89.6 (J = 12.1 Hz), 82.8 (5C), 72.6, 50.8 (J = 113.2 Hz), 51.1, 41.1 (J = 9.1 Hz), 36.5, 36.3 (J = 86.1 Hz), 33.7, 33.3 (J = 6.1 Hz), 29.2, 27.2 (3C), 26.8, 26.5, 26.3, 23.9, 23.5; no characteristic data for the minor exo compound. ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 60.4; (minor) 66.1. **(Endo + Exo) 20b** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 2.28−2.11 (m), 2.06−1.84 (m), 1.68−1.01 (m); IR (C_6D_6) 2920, 2850, 1440, 1360, 1285 cm^{-1}.

Complexes 20c. Yield = 83%. Method A. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 5.82 (d, J = 6.8 Hz, 1H), 4.82 (s, 5H), 2.60 (d, J = 9.2 Hz, 3H), 2.02 (m, 1H), 0.58 (d, J = 6.3 Hz, 3H), 0.09 (ddd, J = 11.7, 6.6, 1.0 Hz, 1H); (minor) 5.83 (d, J = 6.8 Hz, 1H), 4.89 (s, 5H), 2.61 (d, J = 9.3 Hz, 3H), 0.58 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 138.0 (J = 10.1 Hz), 96.4 (J = 10.1 Hz), 92.4 (J = 14.2 Hz), 83.2 (5C), 78.4, 72.9, 61.7 (J = 8.1 Hz), 48.2 (J = 12.1 Hz), 39.2 (J = 93.0 Hz), 33.5 (J = 8.1 Hz), 28.9 (J = 8.1 Hz), 15.3; (minor) 138.3 (J = 10.1 Hz), 96.7 (J = 10.1 Hz), 92.1 (J = 14.2 Hz), 83.6 (5C), 78.3, 72.6, 61.7 (J = 8.1 Hz), 47.9 (J = 10.1 Hz), 39.1 (J = 95.0 Hz), 33.3 (J = 8.1 Hz), 29.1 (J = 6.1 Hz), 15.4. ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 50.2; (minor) 48.3. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 5.73 (d, J = 6.6 Hz, 1H), 4.93 (s, 5H), 2.83 (d, J = 8.8 Hz, 3H), 0.69 (m, 1H), 0.53 (d, J = 6.7 Hz, 3H); (minor) 5.74 (d, J = 6.6 Hz, 1H), 5.01 (s, 5H), 2.84 (d, J = 8.9 Hz, 3H), 1.92 (m, 1H), 0.69 (m, 1H), 0.56 (d, J = 8.7 Hz, 3H), 0.24 (dd, J = 12.7, 7.1 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 138.1 (J = 10.1 Hz), 96.0 (J = 8.1 Hz), 91.5 (J = 14.2 Hz), 82.9 (5C), 78.4, 72.7, 61.5 (J = 6.1 Hz), 43.4 (J = 157.8 Hz), 40.1 (J = 12.1 Hz), 34.1 (J = 8.1 Hz), 29.7 (J = 4.0 Hz), 15.3; (minor) 138.3 (J = 10.1 Hz), 96.3 (J = 8.1 Hz), 91.6 (J = 14.2 Hz), 83.1 (5C), 78.3, 72.6, 61.3 (J = 6.1 Hz), 42.2 (J = 164.0 Hz), 40.1 (J = 12.1 Hz), 34.1 (J = 8.1 Hz), 30.1 (J = 2.1 Hz), 15.0. ^{31}P NMR (162 MHz, C6D6) δ: (major) 49.0; (minor) 47.4. **(Endo + Exo) 20c** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ: 7.29−6.98 (m, 20H), 4.44−4.09 (m), 4.04−3.79 (m), 3.26−3.19 (m), 2.99−0.44 (m); ^{13}C NMR (100 MHz, C_6D_6) δ 128.3 (6C), 127.7 (6C), 126.2 (4C), 126.0 (4C), 37.0, 36.8, 36.7, 36.6, 33.9, 33.7 (2C), 28.5 (2C), 28.1(2C), 27.5 (2C), 27.3 (2C), 26.9, 26.8, 26.7, 26.6 (2C), 26.4, 24.0, 23.9, 23.8, 23.7, 23.6 (2C), 23.5 (2C), 23.3, 23.1, 22.7.

Complexes 20d. Yield = 88%. Method A. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 7.46 (d, J = 7.6 Hz, 2H), 5.28 (d, J = 6.1 Hz, 1H), 4.78 (s, 5H), 2.46 (d, J = 10.2 Hz, 3H), 2.14 (m, 1H), 0.70 (d, J = 6.6 Hz, 3H); (minor) 7.34 (d, J = 7.6 Hz, 2H), 5.30 (d, J = 5.1 Hz, 1H), 4.88 (s, 5H), 2.32 (d, J = 9.6 Hz, 3H), 2.24 (m, 1H), 2.14 (m, 1H), 0.73 (d, J = 6.6 Hz, 3H), 0.03 (ddd, J = 13.0, 7.9, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 138.4, 127.9, 96.4 (J = 8.1 Hz), 92.2 (J = 14.2 Hz), 83.5 (5C), 82.1, 72.3, 59.6 (J = 8.1 Hz), 48.3 (J = 14.2 Hz), 42.4 (J = 153.7 Hz), 32.4 (J = 8.1 Hz), 28.3 (J = 7.1 Hz), 14.7; (minor) 138.5, 128.0, 96.5 (J = 6.1 Hz), 92.0 (J = 16.2 Hz), 83.7 (5C), 81.8, 72.0.3, 59.2 (J = 8.1 Hz), 48.2 (J = 12.1 Hz), 41.8 (J = 159.7 Hz), 32.2 (J = 10.1 Hz), 28.2 (J = 4.0 Hz), 15.0. ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 49.6; (minor) 48.8. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 7.49 (d, J = 7.6 Hz, 2H), 5.25 (d, J = 4.6 Hz, 1H), 4.89 (s, 5H), 2.75 (d, J = 9.1 Hz, 3H), 0.79 (d, J = 6.6 Hz, 3H), 0.75 (m, 1H); (minor) 7.59 (d, J = 7.1 Hz, 2H), 5.24 (d, J = 6.1 Hz, 1H), 5.00 (s, 5H), 2.45 (d, J = 10.2 Hz, 3H), 1.90 (m, 1H), 0.81 (d, J = 5.1 Hz, 3H), 0.65 (m, 1H), 0.13 (ddd, J = 12.7, 7.0, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 138.3, 95.2 (J = 8.1 Hz), 91.4 (J = 14.2 Hz), 83.1 (5C), 82.0, 72.6, 59.9 (J = 8.1 Hz), 42.4 (J = 153.7 Hz), 40.2 (J = 12.1 Hz), 33.1 (J = 8.1 Hz), 29.3 (J = 5.1 Hz), 14.8; (minor) 138.4, 95.5 (J = 6.1 Hz), 91.3 (J = 16.2 Hz), 83.3 (5C), 81.7, 72.5, 59.5 (J = 8.1 Hz), 41.8 (J = 159.7 Hz), 40.0 (J = 10.1 Hz), 32.8 (J = 8.1 Hz), 29.1 (J = 5.1 Hz), 14.2. ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 48.7; (minor) 48.4. **(Endo + Exo) 20d** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 7.26−7.09 (m, 12H), 3.36−3.03 (m), 4.23−4.11 (3t, J = 4.6 Hz, 3H), 3.96−3.80 (4t, J = 5.1 Hz, 4H), 2.94, 1.14 (m), 0.92−0.59 (2m); ^{13}C NMR (100 MHz, C_6D_6) 127.4 (6C), 127.2 (4C), 126.9 (4C), 126.3 (4C), 37.0 (2C), 36.9, 36.8, 36.7, 36.5, 35.8, 34.0 (2C), 33.7 (2C), 28.5, 28.4, 28.3, 28.2, 27.6, 27.3 (2C), 26.8 (2C), 26.7, 26.6 (2C), 26.4, 23.9, 23.8, 23.7, 23.6, 23.5 (2C), 23.3, 23.1.

Complexes 20e. Yield = 100%. Method A. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.72 (s, 5H), 4.20−3.80 (m, 2H), 2.34 (d, J = 9.2 Hz, 6H); (minor) 4.65 (s, 5H), 4.20−3.80 (m, 2H), 2.74 (d, J = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 140.3 (J = 10.1 Hz), 139.6 (J = 4.0 Hz), 97.2 (J = 8.1 Hz), 91.2 (J = 14.2 Hz), 83.3 (5C), 75.4 (J = 6.1 Hz), 74.4 (J = 4.3 Hz), 73.4, 47.9 (J = 11.1 Hz), 45.2 (J = 142.0 Hz), 33.1, 30.3 (6.1 Hz); (minor) 140.3 (J = 10.1 Hz), 139.6 (J = 4.0 Hz), 97.2 (J = 8.1 Hz), 91.0 (J = 14.2 Hz), 84.0 (5C), 75.4 (J = 6.1 Hz), 74.4 (J = 4.3 Hz), 72.9, 48.8 (J = 11.1 Hz), 45.8 (J = 155.0 Hz), 33.1, 31.0. ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 48.3; (minor) 46.3. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.86 (s, 5H), 4.20−3.80 (m, 2H), 2.73 (d, J = 10.4 Hz, 6H), 0.85 (m, 1H); (minor) 4.75 (s, 5H), 4.20−3.80 (m, 2H), 2.54 (d, J = 10.6 Hz, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 139.9 (J = 8.1 Hz), 139.3 (J = 4.0 Hz), 96.5 (J = 10.1 Hz), 90.4 (J = 14.2 Hz), 82.9 (5C), 74.2 (J = 4.1 Hz), 73.7, 73.6 (J = 4.2 Hz), 48.1 (J = 141.6 Hz), 40.6 (J = 11.1 Hz), 32.9, 30.1 (J = 7.1 Hz); (minor) 139.9 (J = 8.1 Hz), 139.3 (J = 4.0 Hz), 95.7 (J = 8.1 Hz), 90.4 (J = 14.2 Hz), 83.7 (5C), 74.2 (J = 4.1 Hz), 73.6 (J = 4.2 Hz), 72.6, 47.3 (J = 145.6 Hz), 41.3 (J = 11.1 Hz), 32.6, 31.3 (J = 4.1 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 47.6; (minor) 45.8. **(Endo + Exo) 20e** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 7.25−6.95 (m, 40H), 2.33−1.10 (m), 0.79−0.32 (m); ^{13}C NMR (100 MHz, C_6D_6) δ 127.8−128.9 (mult, 40C), 37.2, 37.1, 37.0, 36.8, 34.1, 33.8, 33.2, 33.1, 31.7 (2C, J = 8.1 Hz), 29.4 (2C), 27.6, 27.4, 27.2, 27.1, 27.0, 26.9 (2C), 26.8 (2C), 26.7, 26.5, 24.0 (2C), 23.9 (2C), 23.7 (2C), 23.5 (2C), 23.4, 23.3, 23.2, 22.8, 22.7.

Complexes 20f. Yield = 80%. Method A. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.84 (s, 5H), 1.57 (m, 3H), 2.09 (m, 1H); (minor) 4.74 (s, 5H), 1.57 (m, 3H), 2.09 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 95.1 (J = 4.1 Hz), 91.3 (J = 12.1 Hz), 83.0 (5C), 72.3, 48.5 (J = 8.1 Hz), 48.1 (J = 87.0 Hz), 15.2 (J = 64.7 Hz); (minor) 95.1 (J = 4.1 Hz), 91.3 (J = 12.1 Hz), 83.1 (5C), 72.3, 48.1 (J = 87.0 Hz), 48.5 (J = 8.1 Hz), 15.1 (J = 65.1 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 37.5; (minor) 37.7. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.95 (s, 5H), 1.74 (m, 3H), 0.68 (m, 1H), −0.13 (m, 1H); (minor) 4.90(s, 5H), 1.74 (m, 3H), 0.68 (m, 1H), −0.22 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 134.4 (J = 101.1 Hz), 132.3 (2C, J = 10.1 Hz), 131.5, 128.5 (2C, J = 12.1 Hz), 94.8, 94.3 (J = 4.1 Hz), 90.4 (J = 10.1 Hz), 82.6 (5C), 72.0, 48.2 (J = 91.2 Hz), 40.4 (J = 12.1 Hz), 17.2 (J = 74.8 Hz); (minor) 134.4 (J = 101.1 Hz), 94.8, 94.3 (J = 4.1 Hz), 90.4 (J = 10.1 Hz), 82.4 (5C), 71.9, 48.2 (J = 91.2 Hz), 40.1 (J = 12.1 Hz), 17.1 (J = 76.8 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 36.1; (minor) 36.2. **(Endo + Exo) 20f** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 8.04−7.97 (m, 4H), 7.94−7.74 (m, 4H), 7.18−7.02 (m, 12H), 4.18−3.92 (m), 2.04−1.18 (m), 0.66−0.57 (m); ^{13}C NMR (100 MHz, C_6D_6) δ 132.0 (2C, J = 102.1 Hz), 131.9, 131.8, 130.9, 130.8 (2C), 130.6 (4C), 130.3 (4C), 39.1, 36.8 (2C), 36.5, 36.4 (2C), 33.7, 33.6, 33.5, 30.7, 30.1, 29.2, 28.9, 28.6, 28.4 (2C), 28.3, 27.8 (2C), 27.4 (2C), 27.1, 26.7, 26.4 (2C), 26.3, 26.2, 24.1, 23.7 (2C), 23.5 (2C), 23.4 (2C), 23.2 (2C), 18.9, 18.5.

Complexes 20g. Yield = 100%. Method A. **Endo** (characteristic data): ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.75 (s, 5H), 1.97 (m, 1H), 1.30 (d, J = 13.2 Hz, 3H), 1.20 (d, J = 13.2 Hz, 9H), −0.29 (dd, J = 12.2, 7.1 Hz, 1H); (minor) 4.76 (s, 5H), 1.27 (d, J = 13.2 Hz, 3H), 1.20 (d, J = 13.2 Hz, 9H), 1.19 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 97.6 (J = 4.0 Hz),

90.2 (J = 10.1 Hz), 83.5 (5C), 71.6, 49.8 (J = 80.9 Hz), 48.8 (J = 8.1 Hz), 35.3 (J = 62.7 Hz), 34.4, 27.0 (3C), 13.0 (J = 66.7 Hz); (minor) 94.6 (J = 4.0 Hz), 90.4 (J = 10.1 Hz), 83.5 (5C), 71.8, 49.8 (J = 80.9 Hz), 47.7 (J = 10.1 Hz), 35.3 (J = 62.7 Hz), 34.4, 27.1 (3C), 13.0 (J = 66.7 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 55.6; (minor) 55.6. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.87 (s, 5H), 1.49 (d, J = 11.2 Hz, 3H), 1.18 (d, J = 13.2 Hz, 9H), 0.65 (m, 1H), −0.32 (dd, J = 12.7, 7.1 Hz, 1H); (minor) 4.89 (s, 5H), 1.45 (d, J = 11.2 Hz, 3H), 1.18 (d, J = 13.2 Hz, 9H), 0.60 (m, 1H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 97.0 (J = 6.1 Hz), 89.1 (J = 12.1 Hz), 83.3 (5C), 72.4, 53.4 (J = 80.9 Hz), 41.9 (J = 10.1 Hz), 35.3 (J = 62.7 Hz), 34.5, 26.9 (3C), 13.4 (J = 62.7 Hz); (minor) 94.2 (J = 6.1 Hz), 89.8 (J = 10.1 Hz), 83.0 (5C), 71.5, 53.2 (J = 80.9 Hz), 40.1 (J = 10.1 Hz), 35.3 (J = 62.7 Hz), 34.6, 26.8 (3C), 13.4 (J = 62.7 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 55.2; (minor) 55.2. **(Endo + Exo) 20g** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 4.38 (s), 4.34 (s), 4.30 (t, J = 6.6 Hz), 4.08 (td, J = 16.8, 6.6 Hz), 3.97 (m), 2.57−2.38 (m), 2.27−2.05 (m), 1.99−0.79 (m), 0.54−0.28 (m); ^{13}C NMR (100 MHz, C_6D_6) δ 36.8, 36.4 (3C), 33.9, 33.8, 33.5 (2C), 32.9 (2C), 29.1 (2C), 28.9 (2C), 28.3 (2C), 27.3 (2C), 26.8 (2C), 26.6 (2C), 26.4 (2C), 23.9 (2C), 23.8 (2C), 23.5 (2C), 23.4 (2C); IR (C_6D_6) 2920, 2850, 1440, 1360, 1285 cm^{-1}. Anal. Calcd for $C_{24}H_{36}CoOP$: C, 66.97; H, 8.43. Found: C, 66.89; H, 8.49.

Complexes 20h. Yield = 29%. Method A. Very unstable compound. **Endo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.67 (s, 5H), 1.48 (d, J = 12.7 Hz, 3H), 1.18 (d, J = 15.8 Hz, 9H); (minor) 4.38 (s, 5H), 1.47 (d, J = 12.2 Hz, 3H), 1.17 (d, J = 16.8 Hz, 9H). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 59.0; (minor) 60.0. **Exo** (characteristic data). ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 4.90 (s, 5H), 1.59 (d, J = 13.2 Hz, 3H), 1.26 (d, J = 17.8 Hz, 9H); (minor) 4.57 (s, 5H), 1.34 (d, J = 14.8 Hz, 3H), 1.24 (d, J = 14.7 Hz, 9H). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 65.7; (minor) 62.0. **(Endo + Exo) 20h** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 3.54 (t, J = 5.1 Hz), 3.42−2.93 (m), 2.80−2.49 (m), 2.40−0.86 (m); IR (C_6D_6) 2920, 2850, 1440, 1360, 1285, 1140 cm^{-1}.

Complex *endo*-21. Yield = 72%. Method A. Characteristic data. ^{1}H NMR (400 MHz, C_6D_6) δ: (major) 8.17−8.12 (m, 1H), 7.93−7.89 (m, 1H), 7.21 (m, 3H), 7.79 (s, 5H), 4.55 (d, J = 4.6 Hz, 1H), 3.43 (d, J = 12.7 Hz, 1H), 2.04 (tt, J = 11.7, 2.6 Hz, 1H), 1.41 (d, J = 14.8 Hz, 3H), 0.67 (qd, J = 12.2, 3.0 Hz, 2H); (minor) 8.07−8.03 (m, 1H), 7.93−7.89 (m, 1H), 7.21 (m, 3H), 4.58 (s, 5H), 4.27 (d, J = 5.6 Hz, 1H), 3.34 (d, J = 11.7 Hz, 1H), 2.07 (tt, J = 11.0, 2.0 Hz, 1H), 1.82 (d, J = 12.7 Hz, 3H), 0.44 (qd, J = 11.7, 3.0 Hz, 2H). ^{13}C NMR (100 MHz, C_6D_6) δ: (major) 138.1 (J = 95.0 Hz), 131.7, 131.5 (J = 10.1 Hz), 130.7 (J = 3.0 Hz), 128.5 (J = 13.1 Hz), 128.2 (J = 8.1 Hz), 83.3, 82.2 (5C), 77.6 (J = 66.6 Hz), 77.5 (J = 11.1 Hz), 77.1 (J = 6.1 Hz), 49.2, 46.6, 41.0, 37.8, 33.8, 32.8, 31.2, 29.4, 27.9, 27.7, 15.8 (J = 103.1 Hz); (minor) 133.6 (J = 125.4 Hz), 131.9 (J = 9.1 Hz), 131.7, 130.8 (J = 3.0 Hz), 128.3 (J = 11.1 Hz), 127.9 (J = 11.1 Hz), 83.3, 82.1 (5C), 77.9 (J = 10.1 Hz), 77.5 (J = 60.7 Hz), 76.9 (J = 10.1 Hz), 49.6, 46.6, 40.7, 38.1, 33.5, 32.8, 31.0, 30.4, 28.1, 27.6, 17.4 (J = 72.3 Hz). ^{31}P NMR (162 MHz, C_6D_6) δ: (major) 32.3; (minor) 33.1. ***endo*-21** (unattributed): ^{1}H NMR (400 MHz, C_6D_6) δ 1.93−0.95 (m, 28H); IR (C_6D_6) 2920, 2850, 1440, 1300, 1290, 1230, 1195 cm^{-1}.

Acknowledgment. Financial support was provided by CNRS and MRES.

Supporting Information Available: Procedure and full description of compounds **2a**, **2b**, **4a**, **6**−**12**, (*E*)- and (*Z*)-**2c**, **13a**, **13b**, **14f**, **14g**, **15a**−**g**; ^{1}H and ^{13}C NMR spectra for compounds **2a**, **4a**, **13a**, **13b**, **15c**, **15d**; and ^{31}P NMR spectra for **15c** and **15d**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO026212R