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Efficient and Selective Rhodium-Catalyzed Hydrophosphorylation of Dienes

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Abstract: The hydrophosphorylation of a model 1,6-diene having a terminal and an internal alkene function has been investigated. Free radical protocols lead invariably to mixtures of cyclic phosphonate products, due to rapid cyclization of the intermediary radical species. Rhodium catalysis using a cyclic pinacol-derived phosphonate provides an efficient technique for the highly selective (>99%) hydrophosphorylation at the terminal alkene function. *In situ* modification of Wilkinson's complex by addition of 2–50 equivalents (*vs.* Rh) of a monophosphine ($PCy_3 > PPh_3$) or carbene ligand greatly improves the catalyst performances (TON up to 2250 mol phosphonate/mol Rh). An even more efficient system was obtained with 2 equivalents (*vs.* Rh) of the bidentate 1,6-bis(diphenylphosphino)hexane ligand, which affords so far unprecedented high catalytic productivity (TON up to 4 550 mol phosphonate/mol Rh) and activity (TOF up to 250 h^{-1}).

Keywords: dienes; free radicals; homogeneous catalysis; hydrophosphorylation; phosphonates; rhodium

Introduction

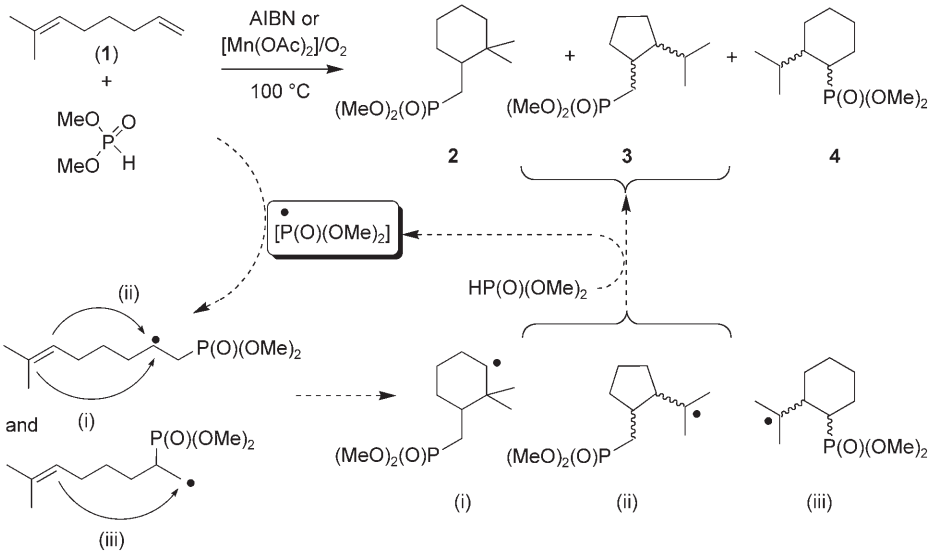
Organophosphonates are important biologically active products[1] and valuable intermediates in fine chemicals synthesis, e.g., *via* Wadsworth–Emmons and related reactions.[2] Also, they can bring special properties to materials, e.g., as flame-retardants in polymers.[3] The traditional method for the preparation of organophosphonates consists in the Arbuzov reaction of phosphites with organic halides.[4] Hydrophosphorylation of alkenes provides a much more atom-economic route toward organophosphonates and usually takes place under relatively mild conditions. Radical initiators have been long known to promote this transformation.[5] However, side-processes associated to such radical promoters in the case of multifunctional substrates[5d] (as further exemplified in this paper) have prompted research into alternative, more selective routes. Recently, several examples of hydrophosphorylation reactions catalyzed by transition metal complexes have been reported.[6,7] In particular, some palladium and rhodium catalysts, mostly based on diphosphine ligands, have emerged for the hydrophosphorylation of terminal and strained alkenes,[8] dienes,[9] as well as allenes,[10] and terminal alkynes.[11] Effective conversion of alkenes to alkylphosphonates with these catalyst systems requires the use of a five-membered cyclic hydrogen phosphonate derived from pinacol (**9**).

In this study we have explored the hydrophosphorylation of 2-methyl-2,7-octadiene (**1**). This commercially available diene, with one terminal and one trisubstituted C=C bond, is a model substrate that mimics pending vinyl groups in a functional polyisoprene which may be used to introduce phosphonate moieties *via* hydrophosphorylation. Our aim was to explore different hydrophosphorylation routes for the selective hydrophosphorylation of the terminal vinyl group.

Results and Discussion

Radical Hydrophosphorylation

Radical hydrophosphorylation of diene **1** was first investigated. The reaction of **1** with 1–5 equivs. of $HP(O)(OMe)_2$, equally promoted by the $Mn(OAc)_2$ (5 mol% vs. **1**)/O_2 system[5d] or AIBN, leads to rapid conversion of **1** to a mixture of products (Scheme 1). As determined by ^{31}P NMR spectroscopy (Figure 1), three products (**2–4**) account for more than 95% of this mixture. Elemental and HR-MS analyses in combination with ^{1}H and ^{13}C NMR spectroscopy estab-



Scheme 1. Radical hydrophosphorylation of diene **1** with $HP(O)(OMe)_2$ and proposed mechanism for the formation of cyclic products **2–4**.

lished that **2–4** are structural isomers that contain a single dimethylphosphonate group but no more double bonds. The formation of 5- and 6-membered cyclic products is easily rationalized, as shown in Scheme 1: the phosphonate radical, generated from AIBN or by its one-electron oxidation of $Mn(OAc)_2/O_2$ system, adds at the terminal or internal vinyl carbons, followed by rapid cyclization of the ene-radical

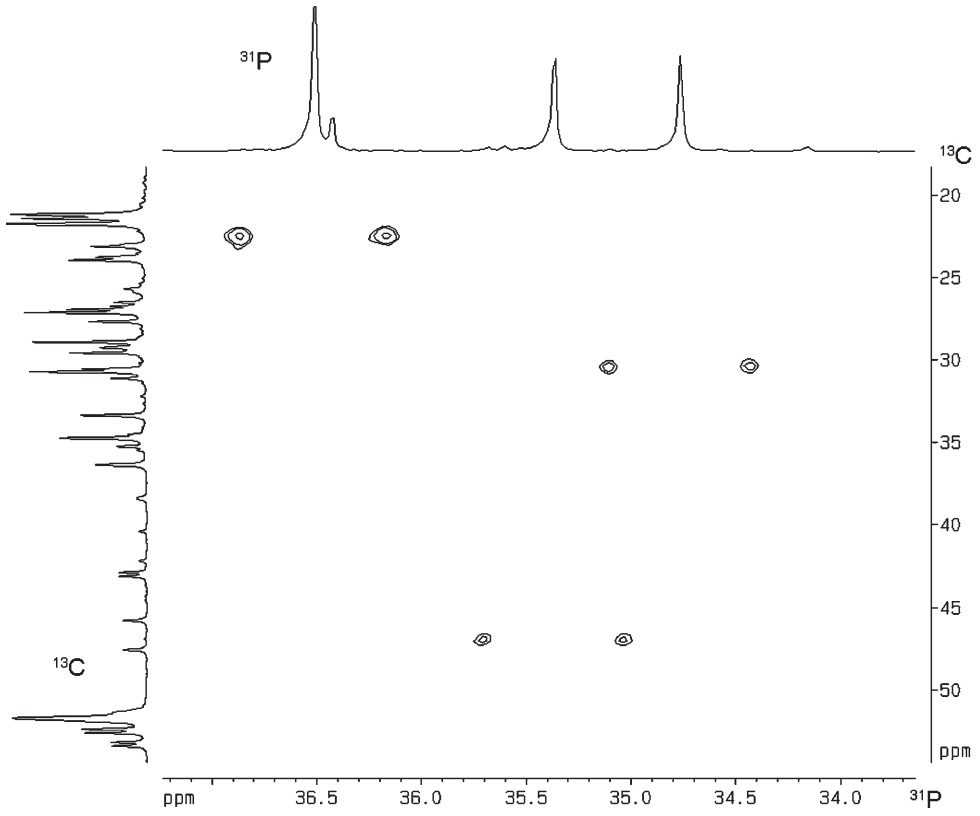


Figure 1. ^{13}C-^{31}P HMQC spectrum ($CDCl_3$, 20 °C) of the mixture of **2–4** [correlations show the $^1J(^{13}C$-$^{31}P)$ coupling constants].

intermediate (i–iii), and subsequent hydrogen transfer from $HP(O)(OMe)_2$ to form **2–4** and regenerate the phosphonate radical.

All attempts to separate products **2–4** by chromatographic techniques have failed so far, most likely due to their close structural similarity. However, combined 1D ^{13}C NMR, DEPT and 2D ^{31}P-^{13}C NMR experiments (see Figure 1, Supporting Information) unambiguously pointed to the Markovnikov product **4** (^{31}P NMR $\delta = 35.37$ ppm, $^{1}J_{P,CH} = 134.1$ Hz; this signal correlates with a CH in the 2D ^{31}P-^{13}C NMR spectrum) in this mixture (25%); the two main other *anti*-Markovnikov products **2** and **3** (^{31}P NMR $\delta = 36.51$, 34.78 ppm; $^{1}J_{P,CH_2} = 138.7$, 140.3 Hz; those signals correlate each with a CH_2 in the 2D ^{31}P-^{13}C NMR spectrum) are formed in 28 and 47% selectivity, but could not be assigned individually (however, since five-membered rings are greatly preferred kinetically over six-membered rings in free radical intramolecular additions on a 5,6-double bond,[12] it may be speculated that **3** is the major product). In fact, the radical hydrophosphorylation of **1** is largely uncontrolled. Similar yields and product distributions were observed upon modification of reaction conditions (temperature, reaction time, reagents and initiator concentrations). Attempted radical hydrophosphorylations of diene **1** with the crowded cyclic phosphonate **9** in place of dimethylphosphonate under a variety of conditions were unsuccessful (see Experimental Section).

The radical hydrophosphorylation of 2,5-dimethyl-1,5-hexadiene (**5**), a symmetric and internally substituted diene, proceeds in a slightly different manner (Scheme 2). When 1 equiv of $HP(O)(OMe)_2$ is used, about twice as much of the monophosphonated alkene **6** (64%) than the cyclopentylphosphonate **7** (36%) are formed. Prevalence of the linear product **6** is best accounted for the usual *anti*-Markovnikov free radical addition,[12] and also by the presence of the 2-methyl substituents, which sterically hinder cyclization of the alkene radical intermediate. On the other hand, with 5 equivs. of $HP(O)(OMe)_2$, the linear diphosphonate product **8** is formed as the sole product (Scheme 2). These results indicate that when larger amounts of $HP(O)(OMe)_2$ are present, hydrogen transfer from H-P(O)$(OMe)_2$ [to regenerate in turn $^{\cdot}P(O)(OMe)_2$] to the alkene radical is favored over cyclization of the latter, and no cyclopentane product **7** is formed. The perfect regioselectivity for terminal addition of $^{\cdot}P(O)(OMe)_2$ radical to alkene functions of **5** to form **6–8** also reflects the strong steric influence of the methyl groups on this reaction.

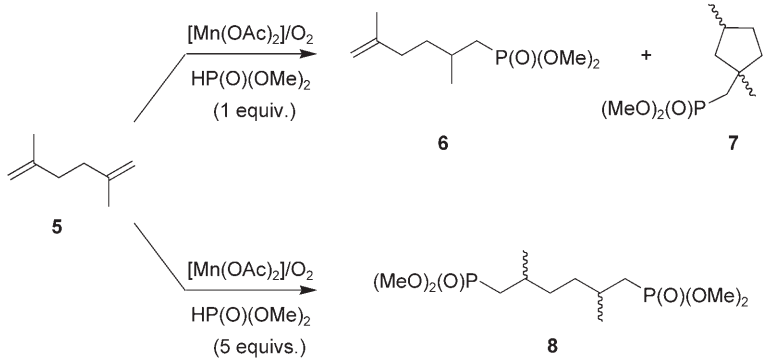
Catalytic Hydrophosphorylation

A series of catalyst precursors based on group VIII metals was subjected to a preliminary screening. Attempts to perform hydrophosphorylation of **1** with simple, acyclic phosphonates $HP(O)(OR)_2$ (R = Me, Et) under a variety of conditions were unsuccessful; in all cases, no products or small amounts of unidentified but P-free by-products were observed. In line with previous reports,[8] high selectivities for hydrophosphorylation were obtained only upon using the pinacol-based phosphonate **9**. Representative results obtained with 2.5 mol% loading of metal catalysts are summarized in Table 1. The reaction of **9** with

Table 1. Metal-catalyzed hydrophosphorylation of 7-methyl-1,6-octadiene (**1**) with phosphonate **9**.[a]

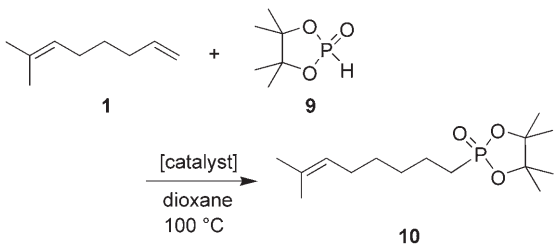
Entry	Precursor	Ligand [equivs.]	Time [h][b]	**10** [%][c]
1	$Pd(OAc)_2$	PPh_3 (2)	20	17
2	$Pd(OAc)_2$	PPh_3 (4)	48	49
3	$Pd(PPh_3)_4$	PPh_3 (2)	24	83
4	$CoCl(PPh_3)_3$	PPh_3 (0 or 2)	18	0
5	$RhCl(PPh_3)_3$	PPh_3 (0)	24	>99
6	$IrCl(COD)_2$	PPh_3 (2)	48	0
7	$IrCl(COD)_2$	PCy_3 (2)	48	0

[a] Metal: 1.50 μmol, **9**: 0.060 mmol, **1**: 0.080 mmol; reaction temperature: 100 °C, solvent: dioxane (1.0 mL).
[b] Reaction time was not necessarily optimized.
[c] Conversion of **9** to **10** as determined by $^{31}P\{^{1}H\}$ NMR.



Scheme 2. Radical hydrophosphorylation of diene **5** at various $HP(O)(OMe)_2$/diene ratios.

1.33 equivs. of diene **1** proceeded smoothly at 100 °C in dioxane with palladium systems and more rapidly with Wilkinson's catalyst, for which reactions readily went to completion within 12 h. However, no activity was detected with related Co- and Ir-based systems. A single product formed in these conditions, i.e., the linear (*anti*-Markovnikov) hydrophosphorylation product of the vinyl bond (**10**), as authenticated by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (Scheme 3). Thus, in this reaction, the catalyst systems operate *via* steric discrimination between the internal (substituted) and terminal olefins. In fact, 2,5-dimethyl-1,5-hexadiene (**5**) proved completely inert under similar catalytic conditions.



Scheme 3.

Previous studies on the transition metal-catalyzed hydrophosphorylation of olefins have highlighted the beneficial effect of diphosphine ligands in terms of phosphonate yield.[8–11] However, none of these studies has explored in detail the impact of added ligand on catalytic activity (TOF) and productivity (TON). As a matter of fact, examples of rhodium-catalyzed hydrophosphorylation of olefins reported so far required large amounts (1.25–5 mol%) of the expensive Wilkinson's complex.[8b,c] We have also explored modification of the simple Wilkinson system by various ligands for the transformation of diene **1** into alkenylphosphonate **10**. The reactions were carried out at high substrate-to-rhodium ratios $\geq$ 400 with the aim to develop truly catalytic systems and to study more easily the influence of added ligands on kinetics. Representative results are reported in Table 2. At this low catalyst loading, the Wilkinson's complex alone does not allow the reaction to reach completion; i.e., about mid-conversion of **9** is attained after 12 h and no more evolution is observed upon longer reaction times, indicating irreversible catalyst decay (entry 1). Addition of PPh_3 (3–50 equivs. vs. Rh) to $RhCl(PPh_3)_3$ improved significantly the turnover and allowed, in turn, full conversion of **9** to **10** (entries 2–5). These results contrast somewhat to those of Pagenkopf and co-workers[8b] who observed no change upon adding 2 equivs. of PPh_3, although at much larger Wilkinson's complex loadings (5 mol%). As apparent from Figure 2, the amount of PPh_3 added has no

Table 2. Hydrophosphorylation of 7-methyl-1,6-octadiene (**1**) by **9** catalyzed by ligand-modified $RhCl(PPh_3)_3$ systems.[a]

Entry	Ligand [equivs.]	[**9**]/[Rh]	Time [h][b]	**10** [%][c]
1	-	400	12	49
2	PPh_3 (2)	400	72	78
3	PPh_3 (10)	400	24	91
4	PPh_3 (50)	400	12	>99
5	PPh_3 (50)	1000	48	38
6	$P(C_6F_5)_3$ (50)	400	12	51
7	$PnBu_3$ (50)	400	12	68(57)
8	PCy_3 (3)	400	8	>99(83)
9	PCy_3 (3)	1000	158	94
10	PCy_3 (50)	1000	72	92
11	PCy_3 (50)	2500	108	90
12	IPr (3)[d]	400	14	92
13	dppb (2)	400	12	89
14	dppb (50)	400	12	95
15	dpph (2)	400	12	93
16	dpph (50)	400	12	>99 (88)
17	dpph (2)	1000	12	96
18	dpph (2)	5000	120[e]	87[e]
19	dchpb (50)	400	12	39

[a] **9**: 0.60 mmol, **1**: 0.80 mmol; reaction temperature: 100 °C, solvent: dioxane (1.0 mL).
[b] Reaction times for >98% conversion were not necessarily optimized.
[c] Conversion of **9** to **10** as determined by $^{31}P\{^{1}H\}$ NMR; Figure in parentheses refer to isolated yields of pure product.
[d] IPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethylimidazol-2-ylidene.
[e] 91% yield after 162 h.

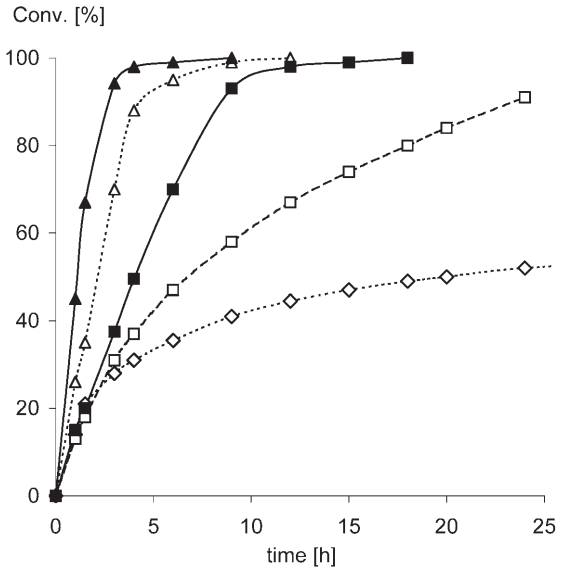


Figure 2. Kinetics of the hydrophosphorylation of **1** with phosphonate **9** promoted by $[RhCl(PPh_3)_3]$/phosphine systems (100 °C, 1,4-dioxane, [**9**]/[Rh] = 400): ▲ PCy_3, 50 equivs. *vs.* Rh, △ PCy_3, 3 equivs., ■ PPh_3, 50 equivs., □ PPh_3, 10 equivs., ◇ PPh_3, 3 equivs.

effect on the *initial* hydrophosphorylation rate, but on the time after which the reaction rate starts to decrease.* In all of these experiments, the progressive formation of $O=PPh_3$ was detected by ^{31}P NMR monitoring. These data suggest that free phosphine (PPh_3) acts, in this reaction, as a reducing agent of oxidized Rh(III) species to regenerate an active catalyst,[13] as previously suggested by Pagenkopf et al. in the case of Rh-dppb systems.[8b] Similar observations were also made with tricyclohexylphosphine as added ligand (*vide infra*).

Contrasted performances were observed by adding other monodentate ligands in place of PPh_3. None or quite modest improvement was gained with $P(C_6F_5)_3$ or $P(n\text{-}Bu)_3$ (entries 6 and 7). On the other hand, addition of the bulky, basic tricyclohexylphosphine to Wilkinson's complex generated a highly active and productive catalyst (entries 8–11). Although only 3 equivs. of PCy_3 vs. Rh already affect positively the system, higher yields in shorter reaction times were again obtained with excess PCy_3 (50 equivs.) (Figure 2 and Figure 3). Considering the high price of this phosphine ligand (as compared to PPh_3), this strategy proved particularly valuable at low rhodium loadings; thus, conversions > 90% could be achieved in reasonable time with as low as 0.04 mol% Rh (entry 11). Although somewhat less efficient than PCy_3, the ubiquitous carbene ligand IPr [IPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethylimadozol-2-ylidene], *in situ* generated by deprotonation of the corresponding imidazolium salt, proved to be also efficient (entry 12). Bulky, strongly σ-donor ligands appear therefore as a new class of efficient monodentate ligands for rhodium-catalyzed hydrophosphorylation of olefins.

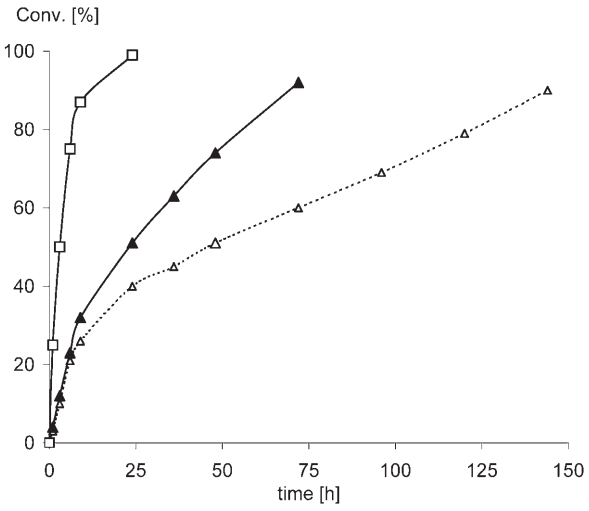


Figure 3. Kinetics of the hydrophosphorylation of **1** with phosphonate **9** promoted by $[RhCl(PPh_3)_3]$/phosphine systems (100 °C, 1,4-dioxane, [**9**]/[Rh] = 1 000): △ PCy_3, 3 equivs. *vs.* Rh, ▲ PCy_3, 50 equivs., □ dpph, 2 equivs.

We obtained the best performances for the hydrophosphorylation of **1** with diphosphine ligands such as dppb or, even better, dpph [dppb = 1,4-bis(diphenylphosphino)butane; dpph = 1,6-bis(diphenylphosphino)hexane] (entries 13–18).** Although a large excess of these chelating ligands may still be beneficial in terms of activity (entries 13–16), it is *not* a prerequisite for high catalyst productivity, contrary to the aforementioned monodentate ligands. The high activity and stability of the catalyst derived from the addition of only 2 equivs. of dpph to Wilkinson's complex is more apparent at very high substrate-to-rhodium ratios (Figure 3). So far unprecedented TOF up to 250 h^{-1} (at 25% conversion) and TON of 4550 mol **1**/mol Rh were thus obtained with this system (entries 17, 18).

A subtle influence of steric and electronic factors was, however, evidenced by the poor performance displayed by 1,4-bis(dicyclohexylphosphino)butane (dchpb, entry 19), a ligand which combines in principle some key properties of PCy_3 and dppb. The high catalytic productivity and activity induced by the two latter ligands likely originate for completely different reasons.

Conclusions

In conclusion, we have shown that rhodium catalysis provides an efficient alternative to free-radical chemistry for the selective hydrophosphorylation of a model 1,6-diene at the terminal alkene function. *In situ* modification of Wilkinson's complex by addition of phosphine or carbene ligands greatly improves the catalyst performances. Adding up to 50 equivs. (vs. Rh) of the simple monodentate tricyclohexylphosphine ligand proved to be quite advantageous, leading to TON up to 2250 mol phosphonate/mol Rh. An even more efficient system was obtained with the bidentate 1,6-bis(diphenylphoshino)hexane ligand, which affords so far unprecedented high catalytic productivity and activity.

[*] The observation of identical initial rates in the presence of 0–50 equivs. of PPh_3 suggests a rate-determining step other than coordination of the olefin bond onto active Rh species, since the latter process is competitive with phosphine coordination.

[**] The use of 1,1-bis(diphenylphosphino)methane (dppm) or 1,2-bis(diphenylphosphino)ethane (dppe) totally inhibited the reaction.

Experimental Section

General Conditions

All manipulations requiring a dry atmosphere were performed under purified argon by use of standard Schlenk techniques or working in a glovebox. Solvents (dioxane, toluene, THF) were freshly distilled from K-Hg amalgam under nitrogen and degassed thoroughly by freeze-thaw-vacuum cycles prior to use. Dienes **1** and **5** and $HP(O)(OMe)_2$ (all purchased from Aldrich) were dried by standard methods and distilled before use. Ligands [PPh_3, PCy_3, $P(C_6F_5)_3$, $P(n\text{-}Bu)_3$, dppb, dpph, dchpb] and complexes [$RhCl(PPh_3)_3$, $Pd(OAc)_2$, $CoCl(PPh_3)_3$, $Pd(PPh_3)_4$, $IrCl(COD)_2$, $Mn(OAc)_2{\cdot}4\ H_2O$] were purchased from Aldrich, ACROS or Strem and used as received. AIBN was purified by recrystallization from diethyl ether and stored in the refrigerator. The cyclic phosphonate **9**[14] and imidazolium salt IPr·HCl[15] were prepared according to the literature.

NMR spectra were recorded on Bruker AC-200 and AC-300 spectrometers at ambient probe temperature. ^1H and ^{13}C NMR chemical shifts are reported in ppm *vs.* $SiMe_4$ and were determined by reference to the residual solvent peaks. Assignment of signals was carried out through multinuclear 1D (^1H, $^{13}C\{^1H\}$, DEPT) and 2D (HMQC, HMBC) NMR experiments. ^{31}P NMR chemical shifts were referenced to external H_3PO_4. EI-HR-MS was performed on a Varian MAT-311 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations.

Radical Hydrophosphorylation of 2-Methyl-2,7-octadiene (1) with $HP(O)(OMe)_2$

In a typical procedure, a solution of $Mn(OAc)_2{\cdot}4\ H_2O$ (36.8 mg, 0.15 mmol) in dimethylphosphonate (990 mg, 9.00 mmol) and 2-methyl-2,7-octadiene (**1**) (372 mg, 3.00 mmol) was magnetically stirred at 100 °C for 2 h under air (1 atm). The mixture was cooled to room temperature and concentrated under vacuum. Flash chromatography (silica, *n*-hexane/ethyl acetate, 1:1) afforded a colorless oil ($R_f = 0.59$, 700 mg, 99 %) as a mixture of **2**, **3** (47 and 28 %) and **4** (25 %). HR-MS (EI): calcd. for $C_{11}H_{23}O_3P$: 234.1385; found: 234.1409.

Compounds **2** and **3**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 20 °C): $\delta = 36.51$, 34.78; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 °C, selected resonances): $\delta = 29.94$ (d, $^1J_{C,P} = 138.7$ Hz, P*C*H_2), 21.94 (d, $^1J_{C,P} = 140.3$ Hz, P*C*H_2).

Compound **4**: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 20 °C): δ 35.37; $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 46.42$ (d, $^1J_{C,P} = 134.1$ Hz, P*C*H).

Compounds **2–4**: ^1H NMR ($CDCl_3$, 200 MHz, 20 °C): $\delta =$ 3.62–3.70 [m, 6 H, $P(O)(OMe)_2$], 0.50–2.30 (m, 17 H).

The same results were obtained when AIBN (37 mg, 0.15 mmol) was used in place of the $Mn(OAc)_2{\cdot}4\ H_2O/O_2$ system.

Attempted Radical Hydrophosphorylations of Diene 1 with Phosphonate 9

Several reactions were carried out as described above with the $Mn(OAc)_2{\cdot}4\ H_2O/O_2$ system, using phosphonate **9** (3 equivs. *vs.* **1**) in place of dimethylphosphonate, in either toluene or dioxane solutions (0.5–3 M) at 100 °C for 2–72 h. In no case could hydrophosphorylation products be detected and phosphonate **9** was the only product observed by ^{31}P NMR spectroscopy.

Radical Hydrophosphorylation of 2,5-Dimethyl-1,6-hexadiene (5) with $HP(O)(OMe)_2$. Synthesis of 1-Dimethylphosphanato-2,5-dimethyl-6-hexene (6) and 1-Dimethylphosphanatomethyl-3,5-dimethyl-cyclopentane (7)

A mixture of $Mn(OAc)_2{\cdot}4\ H_2O$ (20.0 mg, 0.080 mmol), 2,5-dimethyl-1,6-hexadiene (**5**) (176 mg, 1.60 mmol) and $HP(O)(OMe)_2$ (176 mg, 1.60 mmol) was reacted as described above. ^1H NMR of the final oily residue showed complete conversion of **5** to a mixture of **6** and **7** (348 mg, 99 %) in a 64:36 ratio. Flash chromatography (silica, *n*-hexane/ethyl acetate, 1:2) afforded **6** ($R_f = 0.50$, EtOAc; 223 mg, 63 %) and **7** ($R_f = 0.42$, EtOAc; 125 mg, 36 %) as colorless oils.

Compound **6**: ^1H NMR ($CDCl_3$, 300 MHz, 20 °C): $\delta = 4.61$ (d, 2 H, $J_{HP} = 4.5$ Hz, $CH_2=$), 3.64 (d, $J_{HP} = 12.0$ Hz, 6 H, OCH_3), 1.63 (s, 3 H, =C-CH_3), 1.15–2.15 (m, 7 H), 0.98 (d, $J_{HP} = 6.5$ Hz, 3 H, CHCH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 20 °C): $\delta = 35.53$; HR-MS (EI): calcd. for $C_{10}H_{21}O_3P$: 220.1228; found: 220.1230; anal. calcd. for $C_{10}H_{21}O_3P$: C 54.53, H 9.61; found: C 54.28, H 9.88.

Compound 7 (mixture of two diastereomers): ^1H NMR ($CDCl_3$, 300 MHz, 20 °C): $\delta = 3.62$ (d, $J_{H,P} = 12.3$ Hz, 6 H, OCH_3), 1.08–2.05 (m, 12 H), 0.93 (d, $J_{H,P} = 6.7$ Hz, 3 H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 20 °C): $\delta = 35.04$; HR-MS (EI): calcd. for $C_{10}H_{21}O_3P$: 220.1228; found: 220.1226: anal. calcd. for $C_{10}H_{21}O_3P$: C 54.53, H 9.61; found: C 54.65, H 9.92.

Radical Hydrophosphorylation of 2,5-Dimethyl-1,6-hexadiene (5) with $HP(O)(OMe)_2$. Synthesis of 1,6-Dimethylphosphonato-2,5-dimethylhexane (8)

When the above reaction was carried out with 5 equivs. of $HP(O)(OMe)_2$ (880 mg, 8.00 mmol), following the same procedure, compound **8** was obtained as the sole product in the reaction mixture. Flash chromatography (silica, *n*-hexane/ethyl acetate, 1:2) afforded **8** as a colorless oil (348 mg, 99 % yield); R_f 0.33 (EtOAc). ^1H NMR ($CDCl_3$, 300 MHz, 20 °C): $\delta = 3.64$ (d, $J_{H,P} = 10.7$ Hz, 12 H), 1.80–1.10 (m, 10 H), 0.94 (d, $J_{H,P} = 6.3$ Hz, 6 H); ^{31}P NMR ($CDCl_3$, 121.5 MHz, 20 °C): $\delta = 34.60$; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 20 °C) (*ca.* 1:1 mixture of two diastereomers): $\delta = 52.18$–52.03 (several overlapping doublets, O*C*H_3), 35.07 and 34.89 (2 s, *C*H_2), 31.72 and 31.45 (2 d, $^1J_{C,P} = 138.6$ Hz, P-*C*H_2), 28.17 and 28.14 (2 d, $^3J_{C,P} = 5.5$ Hz, *C*H), 20.80 (d, $^1J_{C,P} = 13.1$ Hz, *C*H_3) and 20.70 (d, $^1J_{C,P} = 13.1$ Hz, *C*H_3); HR-MS (EI): calcd. for

$C_{12}H_{28}O_6P_2$: 330.1361; found: 330.1374; calcd. for $[M-CH_3]^+$: 315.1126; found: 315.1159; calcd. for $[M-P(O)(OMe)_2]^+$: 221.1307; found: 221.1320; calcd. for $[M-CH_2P(O)(OMe)_2]^+$: 207.1150; found: 207.1138; anal. calcd. for $C_{12}H_{28}O_6P_2$: C 43.64, H 8.54; found: C 43.76, H 8.42.

Catalytic Hydrophosphorylation of Diene 1 with Phosphonate 9. Synthesis of 4,4,5,5-Tetramethyl-2-(7-methyl-6-octene)-1,3,2-dioxaphospholane 2-Oxide (10)

In a typical procedure, a Schlenk flask was charged with a magnetic stir bar, $RhCl(PPh_3)_3$ (1.4 mg, 1.5 μmol), PCy_3 (1.3 mg, 4.5 μmol) and dioxane (1.0 mL). Phosphonate **9** (98.4 mg, 0.60 mmol) and 7-methyl-1,6-octadiene (100 mg, 0.80 mmol, 1.33 equiv/**9**) were then syringed in. The mixture was stirred in an oil bath at 100 °C for 20 h. After cooling to room temperature, the crude mixture was analyzed by $^{31}P\{^1H\}$ NMR showing > 99 % conversion of **9** to **10**. Volatiles were removed under vacuum and the resulting yellow oil was purified by flash chromatography (SiO_2, EtOAc/hexane, 1:1, $R_f = 0.55$) to give analytically pure **10** as a colorless oil (152 mg, 88 % yield). ^1H NMR ($CDCl_3$, 200 MHz, 20 °C): $\delta = 5.04$ (t, 1H, CH=C), 1.67 (s, 3H, Me), 1.58 (s; 3H, Me), 1.48 (s, 6H, 2Me pinacol), 1.34 (s, 6H, 2Me pinacol), 1.10–2.15 (m, 10H, CH_2); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 20 °C): $\delta = 131.33$ (s, $Me_2C=$), 124.43 (s, =CH), 87.67 (s, O*C*Me$_2$), 30.25 (d, $^3J_{C,P} = 16.7$ Hz, $CH_2CH_2CH_2P$), 29.26 (s, CH_2), 28.07 (d, $^1J_{C,P} = 132.2$ Hz, CH_2P), 27.70 (s, CH_2), 25.66 (s, CH_3), 24.70 (d, $^3J_{C,P} = 3.6$ Hz, OC*Me*$_2$), 24.03 (d, $^3J_{C,P} = 5.2$ Hz, OC*Me*$_2$), 22.77 (d, $^2J_{C,P} = 5.6$ Hz, CH_2CH_2P), 17.61 (s, CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 20 °C): $\delta = 45.30$; HR-MS (EI): calcd. for $C_{15}H_{29}O_3P$ [M^+]: 288.1854; found: 288.1870; anal. calcd. for $C_{15}H_{29}O_3P$: C 62.48, H, 10.14; found: C 62.62, H 10.41.

Specific Hydrophosphorylation Procedure with Carbene Ligand Generated *in situ* from IPr·HCl

In the glovebox, an NMR tube was charged with $RhCl(PPh_3)_3$ (1.4 mg, 1.50 μmol), IPr·HCl (2.1 mg, 4.50 μmol, 3 equivs.) and KO-*t*-Bu (0.5 mg, 4.50 μmol). A solution of phosphonate **9** (98.4 mg, 0.60 mmol) in dioxane (1.0 mL) was added, followed by 7-methyl-1,6-octadiene (100 mg, 0.80 mmol, 1.33 equivs./**9**). The tube was closed, placed in an oil bath at 100 °C and the reaction was periodically monitored by $^{31}P\{^1H\}$ NMR spectroscopy.

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