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ASYMMETRIC CATALYSES

XXXIII *. NEW OPTICALLY ACTIVE PHOSPHOLANES DERIVED FROM TARTARIC ACID **

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Summary

New optically active phospholanes derived from tartaric acid were synthesized by cyclization of 1,4-ditosylates with $NaPH_2$ and Li_2PPh. Alkylation of these phosphines led to stable phosphonium salts which gave the alkylated derivatives on treatment with bases. Phospholanes containing Cl, OMe, or NMe_2 substituents at phosphorus were prepared and characterized. Mn and Rh complexes with alkylphospholane ligands were synthesized. Rh phospholane catalysts gave optical inductions up to 16.8% ee in the enantioselective hydrogenation of (*Z*)-α-(*N*-acetamido)cinnamic acid.

Introduction

With the growing demand for optically pure substances the readily available tartaric acid gained more and more importance as an auxiliary agent for asymmetric synthesis. Its multifunctionality allows structural variations in wide ranges. DIOP, the first chelating diphosphine used in enantioselective catalysis with transition metal complexes, is derived from tartaric acid in 5 steps [2,3]. A large number of phosphines related to DIOP have been synthesized [4] by the same route, in which the COOH groups of tartaric acid are converted into CH_2OTs groups, the tosylate groups of which are replaced by metallated phosphines. Usually the syntheses of the metal phosphides needed for these procedures are tedious, and side reactions lower the yields of the substitution step, especially if alkylphosphides are used.

* For part XXXII see ref. 1.
** Dedicated to Professor J. Tirouflet on the occasion of his retirement.

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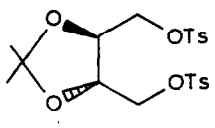
We report here on phosphines of a new type, which are derived from (*R*,*R*)-tartaric acid. These new phosphines contain a stable five-membered phospholane ring, including the two asymmetric carbon atoms of tartaric acid, and a reactive P–H bond which can be used for further derivatization.

Preparation of the phospholanes 3–6

The new phospholanes **3–6**, described here are shown in Scheme 1.

The reaction of the ditosylates **1** and **2** with an excess of $NaPH_2$ in liquid ammonia at $-50\,^{\circ}C$ gives the cyclic phosphines **3a** and **4a**. After substitution of one of the tosylate groups by PH_2^-, cyclization results from an intramolecular attack at the carbon atom bearing the other tosylate group. As in other cyclization reactions, the yields of **3a** and **4a** increase with dilution and reach their maximum (70–75%) at



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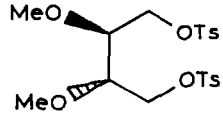

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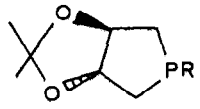
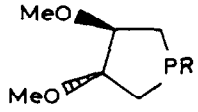
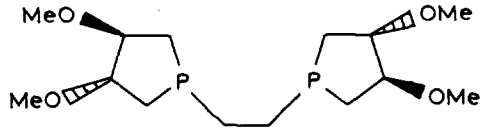




3	a	b
R	H	Ph

4	a	b	c	d	e	f	g	h
R	H	Ph	Cl	NMe_2	OMe	Me	$CH_2C_6H_5$	Li



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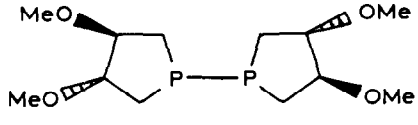


(6)

SCHEME 1

reactant concentrations of ca. 1%. **3a** and **4a** are highly air sensitive colourless liquids. Cyclization reactions of α,ω-dihaloalkanes with primary phosphines or their metallated derivatives are known procedures for the synthesis of phospholanes [5–7].

Phenylphospholanes **3b** and **4b** were prepared in a similar way. Phenylphosphine was metallated in THF with 2 equivalents of n-butyllithium [8]. On addition of the ditosylates **1** or **2**, cyclization occured, to give **3b** and **4b**, respectively.

Because of their reactive P–H bonds, the phospholanes **3a** and **4a** are versatile reagents for variations of the substituents at phosphorus. Chlorination of **3a** and **4a** would be expected to give the P–Cl phospholanes as precursors of P–OR and $P–NR_2$ phospholanes, but in fact, chlorination with phosgene was successful only for **4a**. **4c** was prepared by slow addition of a 20% solution of $COCl_2$ in toluene to **4a** in 83% yield. For **3a** the same procedure gave non-volatile products even when triethylamine (to trap HCl) was present. **4c** is a colourless liquid which fumes in air owing to hydrolysis at the P–Cl bond.

Addition of methanol or dimethylamine to the chlorophospholane **4c** (with a tertiary amine present to take up HCl) gave **4d** and **4e**, respectively. The products are sensitive to air and moisture. The P–N or P–O bond is cleaved by protic reagents.

As expected, the P–H bond of **4a** is acidic towards strong bases. When **4a** is treated with n-BuLi in ether, the Li derivative **4h** separates as a white solid. The dried product is stable but extremely pyrophoric. It reacts with the chlorophospholane **4c** to give the P–P coupling product **6** as a viscous oil.

N-alkylated pyrrolidine analogues of **4f**, **4g**, and **5** were synthesized by heating the ditosylate **2** with the appropriate primary amines [9]. With phospholane systems such as **4a**, alkylation seems to provide a better approach. Because of side reactions, especially metal–halogen exchange, alkylation of the Li derivative **4h** proved to be unsatisfactory for the preparation of P-alkyl derivatives. More successful was a route which involved phosphonium salts as intermediates. Primary or secondary phosphines react with alkyl halides to give phosphonium salts, containing 1 or 2 H atoms at phosphorus. These are sometimes unstable, and lose hydrogen halides to produce the alkylated phosphines or can be isolated and afford free phosphines only on treatment with bases [10,11].

For the preparation of the methyl and benzyl derivatives **4f** and **4g** by the phosphonium salt route, **4a** was treated with methyl iodide or benzyl bromide in methanol. The corresponding phosphonium salts, the synthesis, properties, and spectra of which are described in ref. 12, form stable white solids. The substituted phospholanes **4f** and **4g** were obtained on treatment of the phosphonium salts with 10% aqueous NaOH. **4f** and **4g** are distillable oils.

The compound **5**, containing an ethylene bridge between the two P atoms, was prepared by heating one equivalent of 1,2-dibromoethane with two equivalents of **4a** without solvent. Like **4f** and **4g**, it formed an isolable phosphonium salt, which gave **5** on treatment with 10% aqueous NaOH. Its N-analogue is a distillable liquid, but **5** decomposes at temperatures higher than 100 °C.

Spectroscopy of the phospholanes 3–6

The IR spectra of both **3a** and **4a** contain the ν(P–H) band at 2290 cm^{-1} (film). For all the compounds **3–5** the molecular ions were observed in the mass spectra

TABLE 1

^1H NMR (250 MHz, C_6D_6, int. TMS) AND ^{31}P NMR SPECTRA (101.26 MHz, C_6H_6/C_6D_6 6/1, ext. 85% H_3PO_4) ^1H–^{31}P coupling allowed; δ-values in ppm, coupling constants in Hz

	^1H NMR	^{31}P NMR
3a	1.15–1.70 (m, 4H, CH_2) 1.41, 1.44 (2s, 6H, CH_3) 3.17–3.31 (m, 0.5H, PH) 3.56–3.68 (m, 1H, CH) 3.86–4.06 (m, 1.5H, CH, PH)	−56.60, dm ^1J(PH) 187
4a	1.46–2.02 (m, 4H, CH_2) 3.03, 3.04 (2s, 6H, CH_3O) 3.08–3.30 (m, 1H, PH) 3.67–3.73 (m, 2H, CH)	−95.30, dm ^1J(PH) 181
3b	1.38, 1.44 (2s, 6H, CH_3) 1.71–1.91 (m, 3H, CH_2) 2.10–2.28 (dd, 1H, CH_2) 3.80–3.92 (dquart, 1H, CH) 4.05–4.16 (quart, 1H, CH) 6.98–7.21 (m, 5H, Ar)	12.40, m
4b	1.88–2.34 (m, 4H, CH_2) 3.06, 3.10 (2s, 6H, CH_3O) 3.72 (dt, 1H, CH) 3.87 (quart, 1H, CH) 7.05–7.23 (m, 3H, Ar) 7.50–7.60 (t, 2H, Ar)	−25.60, m
4c	1.94–2.25 (quint, 4H, CH_2) 3.07 (s, 6H, CH_3O) 3.85 (m, 2H, CH)	112.30, m
4d	1.66–2.02 (m, 4H, CH_2) 2.54 (d, 6H, NCH_3) ^3J(PH) 9.3 3.08, 3.10 (2s, 6H, CH_3O) 3.60–3.67, 3.81–3.89 (2m, 2H, CH)	63.40, m
4e	1.59–2.16 (m, 4H, CH_2) 3.11, 3.15 (2s, 6H, CH_3O) 3.20, 3.25 (d, 3H, CH_3OP) ^3J(PH) 13.9 3.60–3.69, 3.98–4.06 (2 quart, 2H, CH)	140.90, m
4f	1.04 (d, 3H, PCH_3) ^2J(PH) 3.3 1.41–2.03 (m, 4H, CH_2) 3.09 (s, 6H, CH_3O) 3.75, 3.89 (2m, 2H, CH)	−42.70, m
4g	1.70–1.94 (m, 4H, CH_2) 2.72–3.00 (m, 2H, $ArCH_2$) 3.02, 3.08 (s, 6H, CH_3O) 3.55–3.90 (m, 2H, CH) 7.02–7.36 (m, 5H, Ar)	−22.7, m

TABLE 1 (continued)

	^{1}H NMR	^{31}P NMR
5	1.56–2.05 (m, 8H, CH_2) 1.93–1.98 (t, 4H, CH_2) 3.06 (s, 12H, CH_3O) 3.73–3.91 (m, 4H, CH)	−27.1, m

(Table 2). The fragmentation patterns, supported by metastable peaks, are discussed in ref. 12.

Compounds **3–5** were characterized by ^{1}H NMR and ^{31}P NMR spectroscopy (Table 1). Ref. 12 contains details of the assignment of the signals and the discussion of the spectra on the basis of spin decoupling experiments. Except for **3a**, all the compounds were found to be spectroscopically pure. The ^{31}P NMR spectrum of **3a** shows an additional signal at −158.2 ppm (intensity ca. 2% of the product signal) which in view of its high field shift can be assigned to a primary phosphine. The ^{31}P NMR and ^{1}H NMR spectra of **3a** and **4a** exhibit the typical doublets due to ^{31}P–^{1}H coupling, demonstrating that **3a** and **4a** are secondary phosphines (Fig. 1).

TABLE 2

ANALYTICAL DATA, MOLECULAR IONS FOUND IN THE MASS SPECTRA, AND OPTICAL ROTATIONS FOR COMPOUNDS **3–6**

Compound	Molecular formula	Mol. weight	*m/e*	Analyses (Found (calc) (%))		$[\alpha]_{578}$ (°) (toluene)
				C	H	
3a	$C_7H_{13}O_2P$	160.14	160	52.25 (52.50)	8.01 (8.18)	+95.1 *c* 0.96
4a	$C_6H_{13}O_2P$	148.13	148	48.41 (48.65)	8.66 (8.71)	+131.3 *c* 0.78
3b	$C_{13}H_{17}O_2P$	236.24	236 [a]	66.19 (66.10)	7.14 (7.25)	–
4b	$C_{12}H_{17}O_2P$	224.23	224	64.25 (64.28)	7.60 (7.64)	–
4c	$C_6H_{12}ClO_2P$	182.58	182	39.50 (39.47)	6.48 (6.62)	+128.7 *c* 0.84
4d	$C_8H_{18}NO_2P$	191.19	191	49.98 (50.25)	9.56 (9.49)	+92.0 *c* 1.12
4e	$C_7H_{15}O_3P$	178.16	178	47.13 (47.18)	8.41 (8.48)	+101.0 *c* 0.97
4f	$C_7H_{15}O_2P$	162.16	162	51.73 (51.90)	9.32 (9.33)	+86.0 *c* 0.85
4g	$C_{13}H_{19}O_2P$	238.25	238	65.60 (65.53)	7.97 (8.04)	–
5	$C_{14}H_{28}O_4P_2$	322.30	322	52.00 (52.17)	8.68 (8.76)	+87.9 *c* 0.43
6	$C_{12}H_{24}O_4P_2$	294.25	–	48.13 (48.97)	8.38 (8.22)	–

[a] Field desorption from toluene.

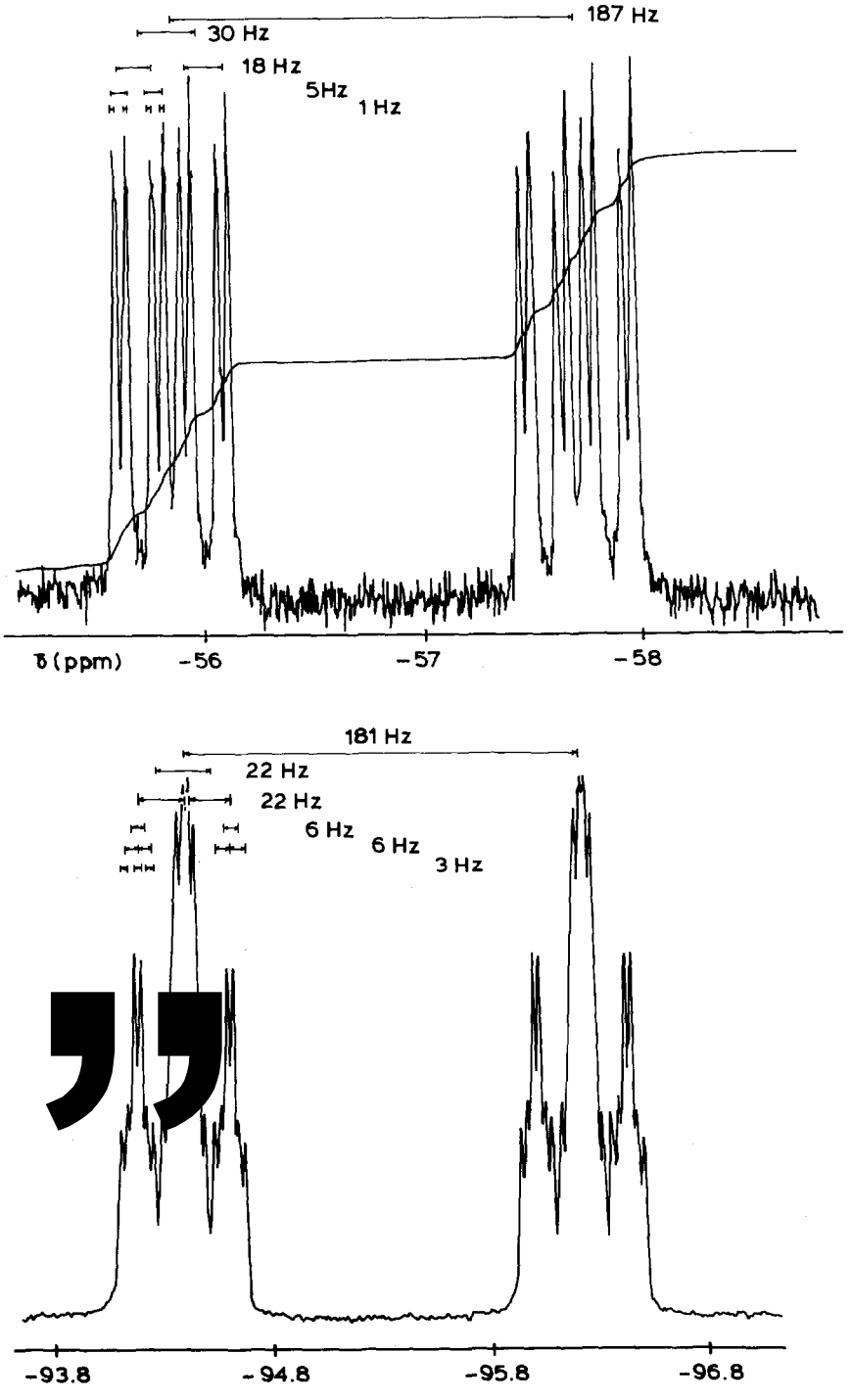
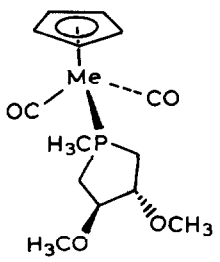


Fig. 1. High resolution ^{31}P NMR spectra of **3a** and **4a**, $^{31}P-^{1}H$ coupling allowed (101.26 MHz, C_6H_6/C_6D_6 6/1, ext. 85% H_3PO_4).



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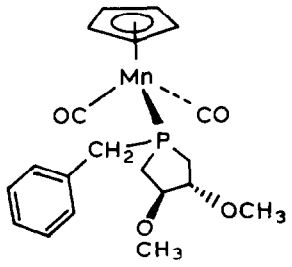
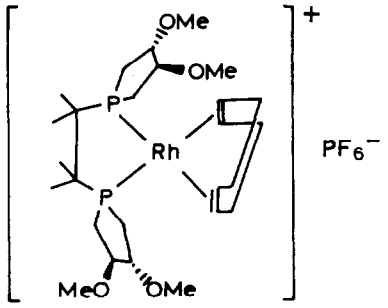


(7g)



(8)

SCHEME 2

Synthesis of Mn and Rh complexes of 4f, 4g and 5 and results of enantioselective catalysis

The Mn complexes **7f** and **7g** (Scheme 2) were prepared by substitution of one CO ligand in tricarbonylcyclopentadienylmanganese (cymantrene) by THF and subsequent treatment with **4f** or **4g**. They are brown, air- and light-sensitive oils, which do not crystallize. When $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) was treated with two equivalents of **5** and NH_4PF_6 by the procedure given in ref. 13, the Rh complex **8** was obtained as an orange air sensitive solid (Scheme 2).

The catalytic hydrogenation of α-*N*-acetamidocinnamic acid with rhodium phospholane complexes was carried out by established methods [14,15]. In all cases 100% hydrogenation was attained. In situ catalysts, prepared from $[Rh(cod)Cl]_2$ and the ligands **4f** and **4g**, gave optical yields of *S*-*N*-acetylphenylalanine of 14.3% ee and 6.6% ee, respectively. The isolated complex **8** used as catalyst yielded 16.8% ee of the *R* product.

Experimental

All reactions were carried out under nitrogen. Solvents were dried by standard methods and saturated with nitrogen.

IR spectra were recorded on a Beckman IR 4240, ^{1}H NMR (60 MHz), ^{1}H NMR (250 MHz) and ^{31}P NMR spectra (101. 26 MHz) on a Varian EM 360 and a Bruker WM 250, ^{13}C NMR spectra on a Bruker WH 90 (22.64 MHz), and mass spectra on a MAT CH 5 and a Varian 311 A spectrometer.

*Synthesis of 7,7-dimethyl-3-phospha-6,8-dioxa-bicyclo[3.3.0]octane (**3a**) and 3,4-dimethoxyphospholane (**4a**)*

A solution of 85 mmol of the ditosylate **1** [3] (40.0 g) or **2** [9] (39.0 g) in 200 ml of THF was added to a solution of $NaPH_2$ in NH_3 at $-50\,^\circ$C, prepared from 248 mmol of Na (5.7 g) in 1 l of liquid ammonia and 0.7 mol of PH_3 [16]. The solution was stirred for 4 h at $-50\,^\circ$C, then the ammonia was slowly evaporated off and 70 ml of water were added to the white residue. Extraction with ether and distillation (**3a**: b.p. 33 °C, 1 Torr; **4a**: b.p. 35 °C, 1 Torr) gave the products as colourless liquids in 70–75% yield (**3a**: 63.75 mmol, 10.2 g; **4a**: 63.75 mmol, 9.4 g).

^{13}C-NMR (C_6D_6, int. TMS): **3a**: δ 11.10 (d, ^1J(PC) 13.2 Hz, CH_2); 15.30 (d, ^{1}J(PC) 15.3 Hz, CH_2); 27.70 (s, CH_3); 85.67 (d, ^2J(PC) 1.9 Hz, CH); 86.16 (d, ^2J(PC) 4.7 Hz, CH); 119.5 (s, $C(Me)_2$). **4a**: δ 21.00 (d, ^1J(PC) 8.3 Hz, CH_2); 21.46 (d, ^1J(PC) 8.3 Hz, CH_2); 56.15 (s, CH_3O); 56.50 (s, CH_3O); 85.86 (d, ^2J(PC) 5.3 Hz, CH); 87.41 (d, ^2J(PC) 4.0 Hz, CH).

*Synthesis of 7,7-dimethyl-3-phenyl-3-phospha-6,8-dioxa-bicyclo[3.3.0]octane (**3b**) and 1-phenyl-3,4-dimethoxyphospholane (**4b**)*

A yellow suspension of dilithiumphenylphosphide [5], prepared from 18.2 mmol (2.0 g) of phenylphosphine and 45.0 mmol of n-butyllithium (30 ml of a 1.5 *M* solution in hexane) in 100 ml of THF, was added dropwise to a solution of the ditosylate **1** (18.2 mmol, 8.6 g) or **2** (18.2 mmol, 8.3 g) in 100 ml of THF at 0 °C. After 1 h stirring, 30 ml of water were added and the products were extracted with ether. Evaporation of the organic solvent left **3b** and **4b** as highly viscous oils, which were purified by distillation at 90–100 °C and 0.01 Torr. Yields: **3b**: 3.64 mmol, 0.8 g (20%); **4b**: 3.64 mmol, 0.8 g (20%).

*Synthesis of 1-chloro-3,4-dimethoxyphospholane (**4c**)*

A 20% solution of phosgene in toluene (20 ml; 40 mmol) was slowly added to a solution of 34 mmol (5.0 g) of **4a** in 40 ml of toluene at 0 °C. Stirring for 24 h followed by evaporation of the solvent and distillation (62–65 °C, 1 Torr) yielded 28.2 mmol, 5.1 g (83%) of **4c**.

*Synthesis of 1-(N,N-dimethylamino)-3,4-dimethoxyphospholane (**4d**)*

To 160 mmol (7.3 g) of dimethylamine in 60 ml of ether, 17.5 mmol (3.2 g) of **4a** were added at $-10\,^\circ$C. After 18 h stirring at 20 °C the precipitated ammonium salts were filtered off and the solvents were removed. Distillation of the colourless liquid (60–64 °C, 1 Torr) gave 14.3 mmol, 2.7 g (82%) of **4d**.

*Synthesis of 1,3,4-trimethoxyphospholane (**4e**)*

Compound **4c** (16.4 mmol, 3.0 g) was added to a vigorously stirred mixture of 49.4 mmol (1.6 g) of methanol, 19 mmol (1.5 ml) of pyridine, and 20 ml of ether at 0 °C. The mixture was allowed to warm to room temperature and stirring was continued for 15 h. Filtration to remove the insoluble pyridinium hydrochloride,

followed by evaporation of the solvent, and distillation (20–30 °C, 0.01 Torr) gave **4e** with 68% (2.0 g, 11.2 mmol) yield.

*Synthesis of 1-methyl-3,4-dimethoxyphospholane (**4f**), 1-benzyl-3,4-dimethoxyphospholane (**4g**) and 1,2-bis-(3,4-dimethoxyphospholano)ethane (**5**)*

The corresponding alkyl halides and **4a** were heated for 15 h under the conditions described below. Evaporation of the solvent and of the volatile reactants in vacuo and subsequent washing left the phosphonium salts as white stable solids.

Without further purification the phosphonium salts were treated during 2 h with a threefold excess of 20% aqueous NaOH with cooling in an ice-bath. The phosphine layer was separated and the colourless oily products purified as described below.

4f: 6.70 mmol (0.95 g) of methyl iodide, 6.75 mmol (1.0 g) of **4a**; solvent: 5 ml of methanol; temp.: 50 °C; distillation of **4f**: b.p. 50–52 °C, 1 Torr. Yield: 0.55 g, 3.39 mmol (50%).

4g: 23.97 mmol (4.1 g) of benzylbromide, 23.65 mmol (3.5 g) of **4a**; solvent: 5 ml of methanol; temp.: 90 °C; distillation of **4g**: b.p. 90–100 °C, 10^{-3} Torr. Yield: 1.85 g, 7.75 mmol (33%).

5: 12.33 mmol (2.3 g) of 1,2-dibromoethane, 24.66 mmol (3.65 g) of **4a**; temp.: 90 °C; purification: dried 18 h at 60 °C, 10^{-4} Torr. Yield: 1.1 g, 3.4 mmol (28%).

*Synthesis of bis-(3,4-dimethoxyphospholane) (**6**)*

A solution of 13.5 mmol (2.0 g) **4a** in 50 ml of ether was treated dropwise with 15.0 mmol of n-butyllithium (1.5 M in hexane) at 20 °C; **4h** precipitated out as a white solid. Addition of 13.5 mmol of **4c** at 0 °C was followed by stirring for 15 h, and then 40 ml of water were added. The organic layer was separated and dried ($CaCl_2$), and the ether was removed to leave **6** as a viscous oil, which was dried at 70 °C at 10^{-4} Torr. Yield: 0.3 g, 1.02 mmol (8%). ^{31}P NMR (C_6D_6/C_6H_6 1/6): δ −37.9 s.

*Synthesis of dicarbonyl-cyclopentadienyl-(1-methyl-3,4-dimethoxyphospholane)-manganese (**7f**) and dicarbonyl-cyclopentadienyl-(1-phenyl-3,4-dimethoxyphospholane)-manganese (**7g**)*

A solution of $C_5H_5Mn(CO)_3$ (cymantrene) in 200 ml of THF was irradiated for 3 h with a Philips HPK 125 W lamp. A solution of the appropriate phospholane in 10 ml of THF was then added, and stirring was continued for 18 h at 20 °C. After evaporation of the solvent the residue was chromatographed on SiO_2 column (protected from light) with toluene/ether (20/1) as eluant. Removal of the solvents left the product as a brown, light-sensitive oil.

7f: 3.33 mmol (0.68 g) of cymantrene, 3.33 mmol (0.54 g) of **4f**. ^{31}P NMR (C_6D_6/C_6H_6 1/6): δ 72.8, s. IR (toluene): ν(CO): 1937, 1870 cm^{-1}. ^1H NMR (60 MHz, C_6D_6, int. TMS): δ 1.4 (d, 3H, PCH_3, ^2J(PH) 8 Hz), 1.6–2.2 (m, 4H, CH_2), 3.0 (s, 6H, CH_3O), 3.8–4.0 (2m, 2H, CH), 4.3 (d, 5H, C_5H_5, ^3J(PH) 3 Hz).

7g: 4.62 mmol (0.94 g) of cymantrene, 4.61 mmol (1.10 g) of **4g**. ^{31}P NMR (C_6D_6/C_6H_6 1/6): δ 83.2, s. IR (toluene): ν(CO): 1935, 1868 cm^{-1}. ^1H NMR (60 MHz, C_6D_6, int. TMS): δ 1.7–2.2, 3.0–4.3 (m, 8H, CH, CH_2), 3.2 (s, 6H, OCH_3), 4.1 (d, 5H, C_5H_5, ^3J(PH) 3 Hz), 7.2 (m, 5H, Ar).

Synthesis of (1,5-cyclooctadiene)-{1,2-bis-(3,4-dimethoxyphospholano)ethane}-rhodium-hexafluorophosphate (8)

A solution of 0.87 mmol (281 mg) of **5** in 2 ml of CH_2Cl_2 was added to a stirred mixture of 0.44 mmol (216 mg) of $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) in 5 ml of CH_2Cl_2 and 1.01 mmol (165 mg) of NH_4PF_6 in 2 ml of water. After 1 h stirring the organic layer was separated and dried ($CaCl_2$). The solvent was evaporated to afford **5** as an orange oil, which crystallized on treatment with pentane. Yield: 427.4 mg, 0.69 mmol (79%). ^{31}P NMR (THF-d_8/THF-h_8 1/7): δ ligand P 62.15, d, ^1J(Rh–P) 157.9 Hz; PF_6 −141.14, quint., ^1J(P–F) 720 Hz.

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