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Polyfunctional phosphine ligands. Preparation of 4′-formyl-2-diphenylphosphinoacetophenone and its coordination properties

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Abstract

The trifunctional ligand [4′-(CHO)C_6H_4]C(O)CH_2PPh_2 (**5**) has been prepared in four steps (overall yield 50%) starting from terephthalaldehyde mono-(diethylacetal) (**1**): reaction of **1** with CH_3MgBr gives [4′-{$CH(OC_2H_5)_2$}C_6H_4]CH(OH)CH_3 (**2**). This is oxidized with MnO_2 to yield the key ketone [4′-{$CH(OC_2H_5)_2$}C_6H_4]C(O)CH_3 (**3**). Metallation of **3** with $LiN[(CH_3)_3Si]_2$ and subsequent reaction with Ph_2PCl affords the phosphine [4′-{$CH(OC_2H_5)_2$}C_6H_4]C(O)CH_2PPh_2 (**4**) which after deprotection of the aldehyde function yields **5**. Condensation of **5** with the *p*-substituted anilines H_2NA-i and H_2NA*-12 gives quantitatively the corresponding phosphine-imines **6**–**9**. Compound **4** reacts instantaneously with [$Pd(acac)_2$] to yield quantitatively the bis-(enolato)-complex *cis*-[Pd{[4′-{$CH(OC_2H_5)_2$}C_6H_4]C(O)=$CHPPh_2$}$_2$] (**10**). Controlled deprotection of **10** gives the corresponding bis-(enolato)-bis-(aldehyde) complex **11**. Reaction of **11** with H_2NA-i and H_2NA*-12 allows the straightforward synthesis of the bis-(enolato)-bis-(imine) complexes **12**–**15**. All compounds have been characterized by elemental analysis, and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR and IR and mass spectroscopy.

Key words: Palladium; Phosphine; Aldehyde; Ketone; Imine

1. Introduction

The recent development of phosphine chemistry is directed mainly towards the synthesis of new multifunctional proligands allowing a subtle control of the physical and chemical properties of transition metal complexes [1]. In such sophisticated systems the phosphorus is usually regarded as the main complexing centre. In most cases, the presence of additional functional groups in phosphines is expected to favour the formation of chelating systems [2] or to create specific binding with substrates coordinated to the metal atom, and thus to facilitate their transformation [3]. In principle, the functional groups may also induce in complexes molecular organization such as mesomorphism or monolayer formation or modify the magnetic and optical properties of complexes. Such aspects have been studied less in phosphine chemistry [4].

One prerequisite for the preparation of phosphine-based molecular materials is the synthesis of polyfunctional phosphines. Of particular interest are heterofunctional phosphines which combine a functional group suitable for metal or substrate binding [5] with a second one displaying a specific physico-chemical, metal-independent, property (*e.g.* solubility [6], mesomorphism, polarizability). To prepare such new multifunctional proligands, we describe herein the synthesis and coordination properties of some new difunctional phosphines derived from the keto-(aldehyde)-phosphine **5**. This compound has a potential (*P,O*) bidentate subunit separated from the aldehyde function by a phenyl spacer. As an illustration of potential synthetic applications of **5** we also describe some reactions involving either the *P,O* function or the aldehyde group. A brief preliminary account of this work has been published [7]. Phosphine ligands which incorporate two distinct functionalities in addition to the phosphorus-(III) are rather rare and have only been studied occasionally in coordination chemistry [8].

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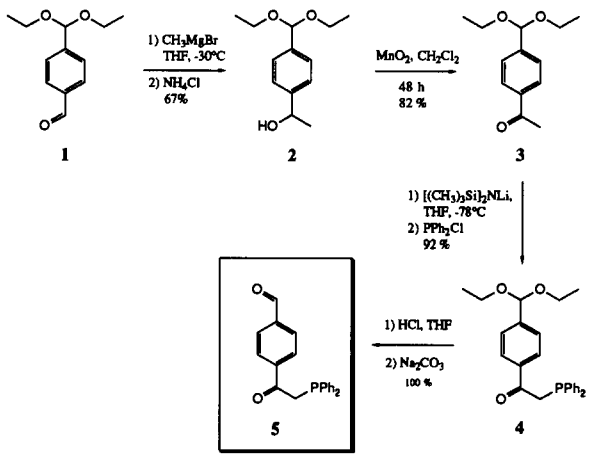


Scheme 1.

2. Results and discussion

2.1. Preparation of 4 and 5

The difunctional compounds **4** and **5** were prepared starting from terephthalaldehyde mono-(diethyl acetal) (**1**) as depicted in Scheme 1.

An aldehyde protective group is required to introduce in three steps a (diphenylphosphino)acetyl subunit. Thus, addition of methylmagnesium bromide to **1** led, after treatment with a weak acid, to the secondary alcohol **2**. Mild oxidation of **2** with MnO_2 in CH_2Cl_2 gave **3** in yields exceeding 80%. Attempts to perform this step by other classical methods such as Swern oxidation [9], Collins oxidation [10], or by means of pyridinium dichromate [11] only gave low yields of the ketone **3**. This is mainly due to side reactions involving the protecting group. Lithiation at −78°C of **3** with lithium hexamethyldisilylamide followed by reaction with chlorodiphenylphosphine gave phosphine **4** almost quantitatively. Treatment of **4** with HCl (1 N) yielded quantitatively the corresponding phosphine aldehyde **5**. Spectroscopic data for these compounds are given in Table 1.

Phosphine **5** may undergo further functionalization using the aldehyde group. Thus, condensation of **5** with the substituted anilines H_2NA-12, H_2NA-16, H_2NA-18 and H_2NA^*-12 (as defined in Scheme 2) gave quantitatively the phosphines **6–9**, respectively (Scheme 2). All these display in their ^1H spectrum a characteristic CH=N signal at *ca.* 8.5 ppm and in their IR spectrum a typical ν(C=N) absorption band at 1626 cm^{-1}.

Each of the compounds **6–9** shows split ν(C=O) bands in the solid state IR spectrum. This is consistent with solid-state interactions, possibly due to hydrogen bonding and to the long-chain substituents. The splitting is not observed in chloroform solutions.

2.2. Preparation of palladium(II) complexes

When two equivalents of the protected phosphine **4** react with $[Pd(acac)_2]$ in CH_2Cl_2, an instantaneous reaction takes place yielding complex **10** (eqn. (1)).

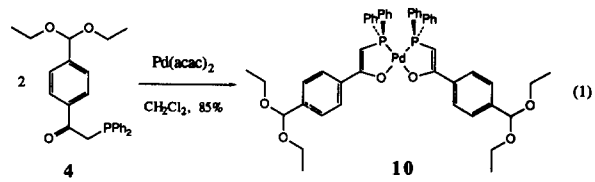
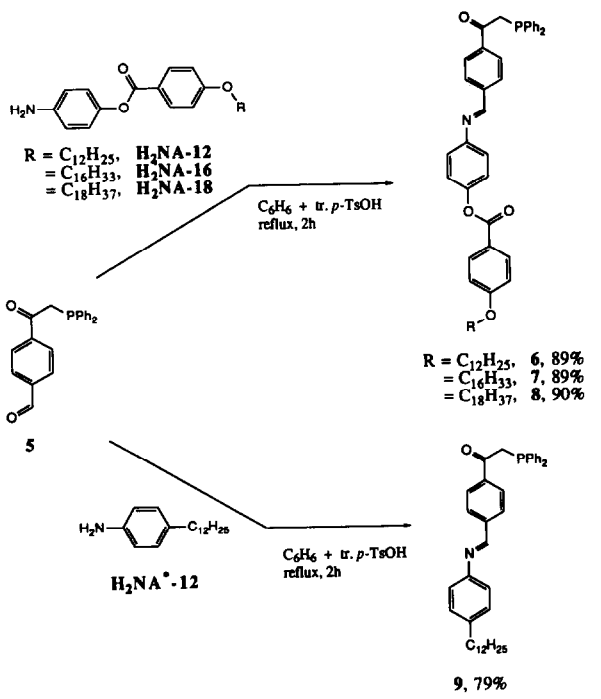


TABLE 1. Selected spectroscopic data for compounds **4–9** [a]

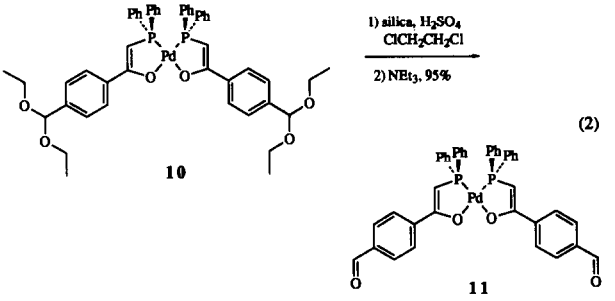
	^1H [b]		^{13}C [b]			^{31}P [c]	IR [d]		
	δPCH_2	δCHN or CHO	$\delta PCH_2(J_{PC})$	$\delta C{=}O(^2J_{PC})$	δC=N or CHO	δ	$\nu(C{=}O)_{keto}$	$\nu(C{=}O)_{ester}$	ν(C=N) or ν(CH=O)
4	3.81	–	40.25(21)	196.50(9)	–	−17.1	1676	–	–
5	3.83	10.09	41.15(24)	196.62(8)	191.45	−16.1	1674	–	1698
6	3.84	8.53	40.98(22)	196.71(8)	158.90	−16.0	1674	1734	1626
							1662	1724	
7	3.84	8.53	40.98(22)	196.66(8)	158.85	−16.2	1674	1736	1626
							1662	1724	
8	3.84	8.53	40.98(22)	196.62(9)	158.85	−16.3	1674	1734	1626
							1662	1722	
9	3.85	8.53	40.81(22)	196.64(8)	157.89	−16.4	1676	–	1626
							1662		

[a] δ in ppm; J in Hz; ν in cm^{-1}. [b] Spectra in $CDCl_3$. [c] Spectra in $CDCl_3$, except for **4** (in THF/C_6D_6) and **9** (in $C_6H_5CH_3/C_6D_6$). [d] KBr pellets, except for **4** (neat).



Scheme 2.

In this reaction a deprotonation occurs which leads to a bis(enolato)-complex. This is confirmed by a typical strong enolate band at 1526 cm^{-1} in the IR spectrum [12,13]. The presence of (i) a doublet for the PCH groups in the ^1H NMR spectrum (δ 4.60, $^2J(PH) = 1.9$ Hz) and (ii) a doublet in the ^{13}C NMR spectrum (δ 78.61, $J(PC) = 64$ Hz) for the corresponding carbon atoms, indicates a *cis* geometry. This stereochemistry has previously been observed in other square planar diphenylphosphino-(enolato)-complexes [14]. Complex **10** may conveniently be converted into the related bis-(aldehyde) complex **11** (eqn. (2)).



(2)

During the first step of the aldehyde deprotection with a H_2SO_4/SiO_2 mixture [15] adsorption of the complex on silica is observed. Upon addition of NEt_3, complex **11** is released. Spectroscopic data (see Table 2) show that the enolate functions are still present and that the *cis* geometry is maintained during this transformation. The aldehyde functions are characterized by a strong ν(C=O) absorption band at 1698 cm^{-1} and a ^1H resonance at 10.02 ppm. Under conditions similar to those described above for the syntheses of **6–9**, complex **11** reacts quantitatively with the amines H_2NA-12, H_2NA-16, H_2NA-18 and H_2NA*-12 to afford the bis(phosphineimine) complexes **12–15** (Scheme 3). As exemplified by Fig. 1, all complexes display well-defined NMR spectra, thus excluding the occurrence of aggregation phenomena in solution due to the long-chain subunits. Spectroscopic data for these com-

TABLE 2. Selected spectroscopic data for complexes **10–15** [a]

	^1H [b]		^{13}C [b]			^{31}P [c]	IR [d]		
	δ PCH($^2J_{PH}$)	δ CHN or CHO	δ PCH(J_{PC})	δ COPd	δ C=N or CHO	δ	ν enol	ν_{ester}	ν imine or aldehyde
10	4.60(1.9)	–	78.61(64)	183.03	–	+37.3	1526 1494	–	–
11	4.75(1.6)	10.02	81.30(63)	181.33	192.13	+37.6	1520 1488	–	1698
12	4.72(< 1)	8.50	80.03(65)	182.39	160.17	+37.5	1510 1496	1722	1624
13	4.74(< 1)	8.50	80.01(63)	182.18	160.19	+37.7	1510 1496	1728	1624
14	4.73(1.5)	8.50	80.02(64)	182.41	160.17	+37.7	1510 1496	1728	1624
15	4.72(1.8)	8.49	79.87(63)	182.01	159.23	+37.5	1520 1500 [e]	–	1626

[a] δ in ppm; J in Hz; ν in cm^{-1}. [b] Spectra in $CDCl_3$. [c] Spectra in $CDCl_3$, except for **10** (in THF/C_6D_6) and **12** (in C_6H_6/C_6D_6). [d] KBr pellets. [e] Not assigned.

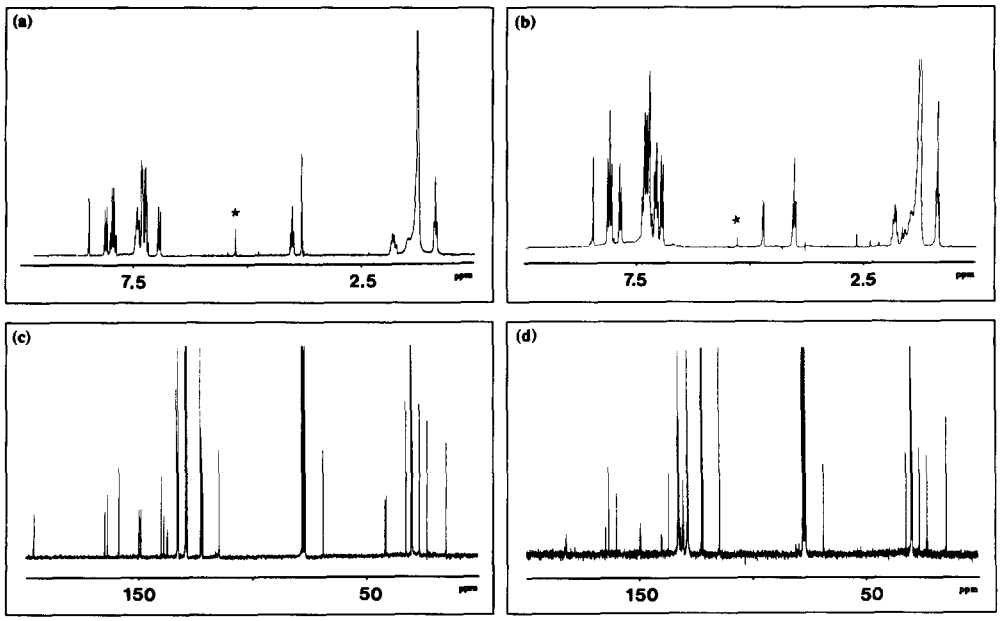
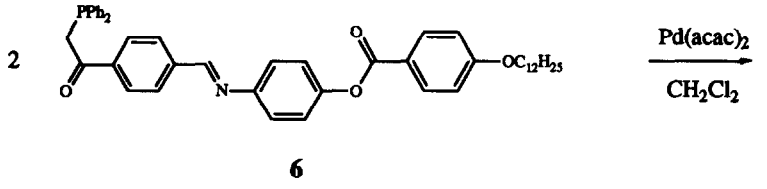


Fig. 1. NMR spectra of compound **8** and complex **14**: (a) ^{1}H NMR spectrum of **8**; (b) ^{1}H NMR spectrum of **14**; (c) $^{13}C\{^{1}H\}$ NMR spectrum of **8**; (d) $^{13}C\{^{1}H\}$ NMR spectrum of **14**. The peaks marked with an asterisk indicate residual CH_2Cl_2.

plexes are given in Table 2. Such complexes may also be obtained by reaction of $[Pd(acac)_2]$ with 2 equiv of the corresponding free phosphine-imine, as shown with phosphine **6** (eqn. 3). No *ortho*-metallated *N,C* compound was formed during this reaction; only deprotonation of the phosphinoacetyl group occurred. This clearly indicates that the first step of the reaction is coordination of the phosphorus atom to the metal.

Complexes **12–15** are yellow, air-stable compounds. They are soluble in common solvents (CH_2Cl_2, THF, toluene) and may be easily chromatographed on silica gel. For none of the phosphines and complexes described above is mesogenic behaviour observed. This is rather surprising for those compounds which contain the alkyl or alkoxy chains derived from H_2NA-12, H_2NA-16, H_2NA-18 and H_2NA*-12, fragments which



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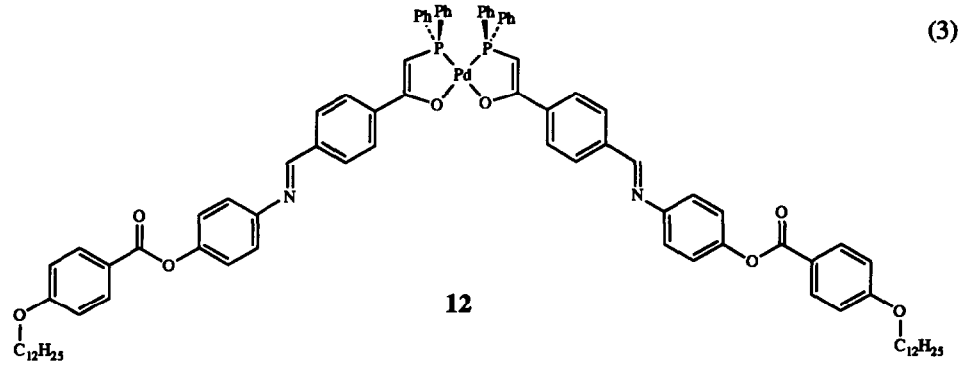

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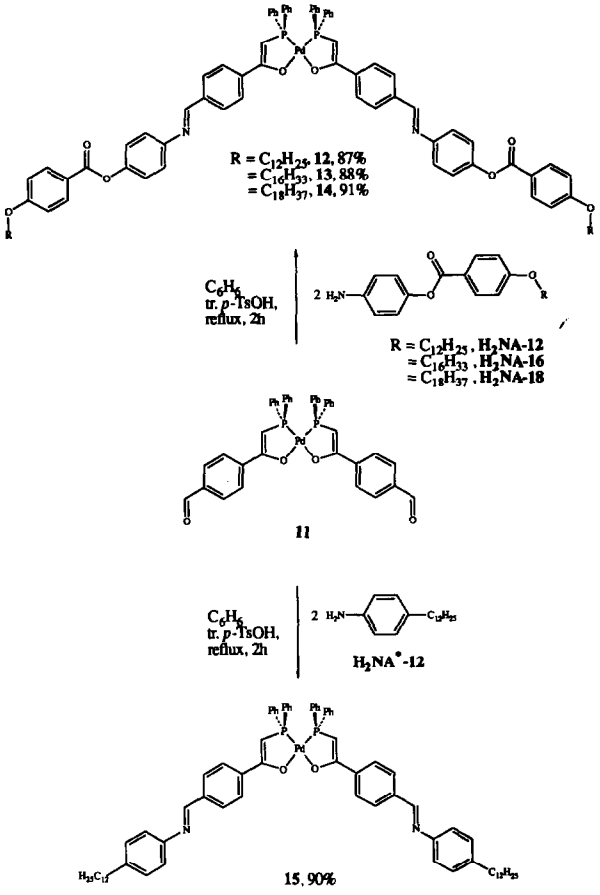
(3)



Scheme 3.

have frequently been reported to induce liquid crystalline behaviour [16]. This could be due to the bulkiness of the phosphino-groups, which does not favour three-dimensional molecular organization.

In conclusion, this work describes a convenient synthesis of a ketophosphine bearing an additional reactive aldehyde function. As an illustration of its multifunctionality it has been (i) condensed with long chain substituted *p*-anilines to afford imino-compounds suitable for metal complexation and (ii) allowed to react with palladium to lead to *P,O* chelate complexes. In subsequent work, we will focus on the reactivity of the aldehyde function to prepare new organometallic materials displaying specific physical properties. The question of whether modification of the substituents at P will facilitate the formation of metallomesogens is also currently under investigation.

3. Experimental details

3.1. General

All reactions were carried out under dry argon by using Schlenk-tube techniques. Solvents, including $CDCl_3$, were dried over suitable reagents and freshly distilled under argon before use. IR spectra were recorded on a IFS 25 Bruker spectrometer. The ^1H NMR data were referenced to residual protonated solvents (7.25 ppm for $CDCl_3$); ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm) and the ^{31}P NMR data are given relative to external 85% H_3PO_4. The ^{13}C NMR chemical shifts marked with an asterisk correspond to signals which could not be assigned unambiguously. The mass spectra of compounds **2–5** and **9** were recorded on a LKB 9000 S mass spectrometer; those of compounds **6** and **7** were recorded on a TSQ70 Finnigan MAT and those of compounds **8**, **10–15** were recorded on a ZAB HF VG Analytical using *m*-nitrobenzyl alcohol as matrix. The silica gel used for chromatography was pre-treated with a 5% NEt_3/THF mixture. $[Pd(acac)_2]$ [17] and the amine precursors O_2NA-12, O_2NA-16 and O_2NA-18, defined in Scheme 2, were prepared according to literature procedures [18]. Amine H_2NA^*-12 (see Scheme 2) is commercially available. The n-BuLi solutions were titrated according to ref. 19.

3.2. Preparation of H_2NA-12

A solution of 4-nitrophenyl-4'-dodecylbenzoate (1.000 g, 2.34 mmol) in CH_2Cl_2/EtOH (20/40 ml) was hydrogenated with vigorous shaking during 24 h, under 4.5 atm of H_2, in the presence of Pd/C 10% (0.150 g). The suspension was then filtered over Celite and the solvent removed *in vacuo*. The product was chromatographed on a silica gel column using a mixture of ethylacetate/hexane (1:2, v/v) as eluant ($R_f = 0.18$). The product was recrystallized from CH_2Cl_2/EtOH and obtained as a white solid (0.858 g, 87%). m.p. 86–88°C. IR (KBr): ν = 3456m, 3427m, 3340m, 3214w, 2955sh, 2920s, 2900sh, 2852s, 1726s ($(C{=}O)_{ester}$), 1606s (NH_2 scissor) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.12–6.70 (m, 8H, aromatic H), 4.03 (t, 2H, OCH_2, $^3J(HH) = 7$ Hz), 3.65 (s, 2H, NH_2 exchanged with D_2O), 1.82 (m, 2H, OCH_2CH_2), 1.47 (m, 2H, $OCH_2CH_2CH_2$), 1.27 (broad s, 16H, CH_2), 0.89 (t, 3H, CH_3, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 165.33*, 163.26*, 144.10*, 143.07*, 132.02*, 122.20*, 121.79*, 115.52*, 114.11*, 68.17 (OCH_2), 31.80*, 29.52*, 29.47*, 29.24*, 28.99*, 25.86*, 22.56*, 13.99 (Me). MS (E.I.), m/z(%) = 397 (100) $[M^+]$. Anal. Found: C, 75.42; H, 8.89; N, 3.47. $C_{25}H_{35}NO_3$ (397.56) calcd.: C, 75.53; H, 8.87; N, 3.52%.

3.3. Preparation of H_2NA-16

This amine was prepared starting from 4-nitrophenyl-4'-hexadecylbenzoate and using a procedure similar to that used for amine H_2NA-12 (yield 87%). m.p. 95–97°C. IR (KBr): ν = 3454m, 3425m,

3341m, 3213w, 2954sh, 2918s, 2851s, 1727s ($(C{=}O)_{ester}$), 1607s (NH_2 scissor) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.12–6.70 (m, 8H, aromatic H), 4.03 (t, 2H, OCH_2, $^3J(HH) = 7$ Hz), 3.64 (s, 2H, NH_2 exchanged with D_2O), 1.81 (m, 2H, OCH_2CH_2), 1.47 (m, 2H, $OCH_2CH_2CH_2$), 1.26 (broad s, 24H, CH_2), 0.88 (t, 3H, CH_3, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 165.39*, 163.18*, 143.95*, 142.99*, 132.05*, 122.26*, 121.86*, 115.56*, 114.15*, 68.23 (OCH_2), 31.84*, 29.59*, 29.50*, 29.27*, 29.04*, 25.89*, 22.60*, 13.99 (Me). MS (E.I.), $m/z(\%) = 453$ (100) $[M^+]$. Anal. Found: C, 76.63; H, 9.37; N, 3.01. $C_{29}H_{43}NO_3$ (453.64) calcd.: C, 76.78; H, 9.55; N, 3.09%.

3.4. Preparation of H_2NA-18

This amine was prepared starting from 4-nitrophenyl-4'-octadecylbenzoate and using a procedure similar to that used for amine H_2NA-12 (yield 74%). m.p. 98–99°C. IR (KBr): ν = 3453m, 3426m, 3342m, 3213w, 2951sh, 2918s, 2851s, 1725s ($(C{=}O)_{ester}$), 1606s (NH_2 scissor) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 8.12–6.70 (m, 8H, aromatic H), 4.03 (t, 2H, OCH_2, $^3J(HH) = 7$ Hz), 3.64 (s, 2H, NH_2 exchanged with D_2O), 1.81 (m, 2H, OCH_2CH_2), 1.47 (m, 2H, $OCH_2CH_2CH_2$), 1.26 (broad s, 24H, CH_2), 0.88 (t, 3H, CH_3, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 165.44*, 163.37*, 144.15*, 143.18*, 132.13*, 122.32*, 121.89*, 115.64*, 114.22*, 68.28 (OCH_2), 31.92*, 29.68*, 29.59*, 29.35*, 29.11*, 25.98*, 22.68*, 14.08 (Me). MS (E.I.), $m/z(\%) = 481$ (100) $[M^+]$. Anal. Found: C, 77.01; H, 9.68; N, 2.84. $C_{31}H_{47}NO_3$ (481.72) calcd.: C, 77.29; H, 9.83; N, 2.91%.

3.5. Synthesis of 1-(4-diethylacetalphenyl)ethanol (2)

A. 3.0 M solution of CH_3MgBr (40.0 ml, 120.0 mmol) was added dropwise within 2.5 h to a solution of terephthalaldehyde mono-(diethylacetal) (**1**) (24.991 g, 120.0 mmol) in THF (200 ml) at −30°C. After stirring for 15 h, a saturated NH_4Cl solution (*ca.* 30 ml) was slowly added to the reaction mixture. The THF was then removed *in vacuo* and Et_2O (150 ml) was added to the mixture. The organic layer was separated and dried over magnesium sulfate. After filtration and evaporation, the product was flash chromatographed on a silica gel column (230-400 mesh) using a mixture of Et_2O/hexane (1:3) as eluant ($R_f = 0.21$). The product was obtained as a pale yellow liquid (18.034 g, 67%). IR (neat): ν = 3378ms cm^{-1} (OH). ^1H NMR ($CDCl_3$): δ = 7.42–7.29 (AA'BB' spin system, 4H, aromatic H), 5.44 (s, 1H, $CH(OC_2H_5)_2$), 4.80 (q, 1H, CH(OH), $^3J(HH) = 6$ Hz), 3.53 (m, 4H, OCH_2), 2.82 (s, 1H, OH), 1.42 (d, 3H, CH_3C(OH), $^3J(HH) = 6$ Hz), 1.20 (t, 6H, CH_3CH_2, $^3J(HH) = 6.5$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 145.96*, 137.91*, 126.56*, 125.09*, 101.23 ($CH(OEt)_2$), 69.77 (CH(OH)), 60.85 (OCH_2), 25.06 (CH_3C(OH)), 15.02 (s, CH_2CH_3). MS (GC, with $CF_3C(O)N(Me)(SiMe_3)$ as sylilating agent), $m/z(\%) = 296$ (1) $[M^+ + SiMe_3]$. Anal. Found: C, 69.43; H, 8.86. $C_{13}H_{20}O_3$ (224.30) calcd.: C, 69.61; H, 8.99%.

3.6. 4'-Diethylacetal-acetophenone (3)

A mixture of MnO_2 (7.982 g, 91.81 mmol) and **2** (4.026 g, 17.95 mmol) in CH_2Cl_2 (125 ml) was stirred for 48 h at room temperature. The suspension was filtered and the solution evaporated to dryness. The residue was then purified by flash chromatography using Et_2O/hexane (1:4) as eluant ($R_f = 0.30$). Compound **2** was obtained as a pale yellow liquid (3.300 g, yield 82%). IR (neat): ν = 1686s cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ = 7.98–7.55 (AA'BB' spin system, 4H, aromatic H), 5.54 (s, 1H, $CH(OEt)_2$), 3.57 (m, 4H, OCH_2), 2.61 (s, 3H, $C(O)CH_3$), 1.24 (t, 6H, CH_2CH_3, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 197.41 (C=O), 143.93*, 136.74*, 127.96*, 126.67*, 100.54 ($CH(OEt)_2$), 60.85 (OCH_2), 26.35 ($CH_3C(O)$), 14.92 (CH_2CH_3). MS (E.I.), $m/z(\%) = 222$ (0.5) $[M^+]$. Anal. Found: C, 70.16; H, 8.11. $C_{13}H_{18}O_3$ (222.28) calcd.: C, 70.24; H, 8.16%.

3.7. 4'-Diethylacetal-2-diphenylphosphino-acetophenone (4)

A 1.54 M solution of *n*-BuLi/hexane (2.9 ml, 4.50 mmol) was added slowly to a solution of hexamethyldisilazane (0.726 g, 4.50 mmol) in THF (15 ml) at −78°C. After stirring the mixture for 0.5 h, a solution of 4'-diethylacetal-acetophenone (**3**) (1.000 g, 4.50 mmol) in THF (10 ml) was added dropwise. The mixture was stirred for 2.5 h while maintaining the temperature at −78°C; it was then transferred to a Schlenk flask containing a solution of PPh_2Cl (0.993 g, 4.50 mmol) in THF (10 ml). The solution was stirred at room temperature for 12 h. The solvent was removed *in vacuo*. The residue was treated with toluene, and the resulting suspension was filtered through a glass frit. Evaporation of the filtered solution gave a pale yellow oil which was chromatographed using AcOEt/hexane (1:4) as eluant ($R_f = 0.38$). This chromatography must be performed carefully in order to separate **4** from unreacted starting compound (R_f = 0.40) (1.72 g, 94%). IR (neat): ν = 1676s cm^{-1} (C=O). ^1H NMR ($CDCl_3$): δ = 7.98–7.31 (14 H, aromatic H), 5.54 (s, 1H, $CH(OEt)_2$), 3.81 (s, 2H, PCH_2, $^2J(PH) = 0$ Hz), 3.58 (m, 4H, OCH_2), 1.25 (t, 6H, OCH_2CH_3, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 196.50 (d, C=O, $^2J(PC) = 8.5$ Hz), 143.90–124.97) (aromatic C's), 100.37 (s, $CH(OEt)_2$), 60.66 (s, OCH_2), 40.25 (d, PCH_2, $J(PC) = 21.3$ Hz), 14.90 (s, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (THF-C_6D_6): δ −17.1 (s). MS (E.I.), $m/z(\%) = 406$ (100) $[M^+]$. Anal. Found: C, 73.67; H, 6.53. $C_{25}H_{27}O_3P$ (406.46) calcd.: C, 73.88; H, 6.70%.

3.8. 4'-Formyl-2-diphenylphosphino-acetophenone (5)

A solution of phosphine **4** (0.406 g, 1.00 mmol) in THF (20 ml) was treated with aqueous HCl (1 N solution, 3 ml). After stirring for 0.5 h, degassed aqueous Na_2CO_3 (0.03 M, 100 ml) was added. The white product was filtered off and dried *in vacuo* (0.315 g, 95%). m.p. 103–104°C. IR (KBr): ν 1698 ms ($C{=}O_{ald}$), 1674 s cm^{-1} ($C{=}O_{keto}$). ^1H NMR ($CDCl_3$): $\delta = 10.09$ (s, HC(O)), 8.08–7.32 (14H, aromatic H's), 3.83 (s, 2H, PCH_2, $^2J(PH) = 0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 196.62 (d, C=O, $^2J(PC) = 7.5$ Hz), 191.45 (s, CH(O)), 141.28–128.67 (aromatic C's), 41.15 (d, PCH_2, $J(PC) =$ 24 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -16.1$ (s). MS (E.I.), $m/z(\%) = 332$ (100) [M^+]. Anal. Found: C, 76.13; H, 5.26. $C_{21}H_{17}O_2P$ (332.34) calcd.: C, 75.90; H, 5.16%.

3.9. N-[4-(2-Diphenylphosphinoacetyl)benzylidene]-4-[4-(dodecyloxy)oxycarbonylphenyl]aniline (6)

This was prepared by treating a benzene solution (25 ml) containing phosphine **5** (0.040 g, 0.12 mmol), H_2NA-12 (0.048 g, 0.12 mmol) and *p*-toluenesulfonic acid (0.001 g, 0.003 mmol) under reflux in a Dean-Stark apparatus during 2 h. The solution was then filtered and concentrated to *ca.* 1 ml. Addition of pentane gave **6** as a white precipitate (0.076 g, 89%). m.p. 110.2–111.2°C. IR (KBr): $\nu = 1734$ms and 1724ms ($C{=}O_{ester}$), 1674s and 1662s ($C{=}O_{keto}$), 1626m (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.53$ (s, 1H, C(H)=N), 8.19–6.96 (22H, aromatic H's), 4.05 (t, 2H, OCH_2, $^3J(HH) = 6.5$ Hz), 3.84 (s, 2H, PCH_2, $^2J(PH) = 0$ Hz), 1.81 (m, 2H, OCH_2CH_2), 1.47 (m, 2H, CH_2), 1.28 (broad s, 16H, CH_2), 0.89 (t, 3H, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 196.71$ (d, $C{=}O_{keto}$, $^2J(PC) = 8$ Hz), 165.02*, 163.74*, 158.90 (s, C=N), 149.88–114.45 (aromatic C's), 68.47 (s, OCH_2), 40.98 (d, PCH_2, $J(PC)$ = 22 Hz), 31.98–14.14 (aliphatic C's). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.0 (s). MS (E.I.), $m/z(\%) = 711$ (1.8) [M^+]. Anal. Found: C, 77.80; H, 7.03; N, 1.98. $C_{46}H_{50}NO_4P$ (711.88) calcd.: C, 77.61; H, 7.08; N, 1.97%.

3.10. N-[4-(2-Diphenylphosphinoacetyl)benzylidene]-4-[4-(hexadecyloxy)oxycarbonylphenyl]aniline (7)

This was prepared using a procedure similar to that used for phosphine **6**, starting from H_2NA-16 (yield 89%). m.p. 109.6–110.6°C. IR (KBr): ν 1736ms and 1724ms ($C{=}O_{ester}$), 1674s and 1662s ($C{=}O_{keto}$), 1626m (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.53$ (s, 1H, CH=N), 8.18–6.96 (22H, aromatic H), 4.05 (t, 2H, OCH_2, $^3J(HH) = 7$ Hz), 3.84 (s, 2H, PCH_2, $^2J(PH) = 0$ Hz), 1.80 (m, 2H, OCH_2CH_2), 1.47 (m, 2H, $OCH_2CH_2CH_2$), 1.26 (24H, CH_2), 0.88 (t, 3H, CH_3, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 196.66$ (d, $C{=}O_{keto}$, $^2J(PC) = 8$ Hz), 164.95*, 163.74*, 158.85 (s, C=N), 149.92–114.49 (aromatic C's), 68.47 (s, OCH_2), 40.98 (d, PCH_2, $J(PC) = 22$ Hz), 31.98–14.08 (aliphatic C's). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -16.2$ (s). MS (E.I.), $m/z(\%) = 767$ (0.5) [M^+]. Anal. Found: C, 78.07; H, 7.34; N, 1.79. $C_{50}H_{58}NO_4P$ (767.99) calcd.: C, 78.20; H, 7.61; N, 1.82%.

3.11. N-[4-(2-Diphenylphosphinoacetyl)benzylidene]-4-[4-(octadecyloxy)oxycarbonylphenyl]aniline (8)

This was prepared starting from H_2NA-18 and using a procedure similar to that used for phosphine **6** (yield 90%). m.p. 110.0–111.7°C. IR (KBr): $\nu = 1734$ms and 1722ms ($C{=}O_{ester}$), 1674s and 1662s ($C{=}O_{keto}$), 1626m (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.53$ (s, 1H, C(H)=N), 8.18–6.96 (22H, aromatic H's), 4.05 (t, 2H, OCH_2, $^3J(HH) = 6.5$ Hz), 3.84 (s, 2H, PCH_2, $^2J(PH) = 0$ Hz), 1.81 (m, 2H, OCH_2CH_2), 1.47 (m, 2H, CH_2), 1.26 (broad s, 28H, CH_2), 0.88 (t, 3H, CH_3, $^3J(HH) = 6$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 196.62$ (d, $C{=}O_{keto}$, $^2J(PC) = 9$ Hz), 164.99*, 163.73*, 158.85 (s, C=N), 149.88–114.47 (aromatic C's), 68.47 (s, OCH_2), 40.98 (d, PCH_2, $J(PC) = 22$ Hz), 31.98–14.11 (aliphatic C's). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -16.3$ (s). MS (FAB), m/z (%) = 796 (15) [$(M + H)^+$]. Anal. Found: C, 78.44; H, 8.14; N, 1.73. $C_{52}H_{62}NO_4P$ (796.04) calcd.: C, 78.46; H, 7.85; N, 1.76%.

3.12. N-[4-(2-Diphenylphosphinoacetyl)benzylidene]-4-(dodecyl)aniline (9).

This was prepared by heating a benzene solution (25 ml) containing phosphine **5** (0.050 g, 0.15 mmol), H_2NA^*-12 (0.039 g, 0.15 mmol) and *p*-toluenesulfonic acid (0.001 g, 0.003 mmol) under reflux in a Dean-Stark apparatus during 2 h. The solution was then filtered and concentrated to *ca.* 1 ml. Addition of methanol gave **9** as a pale yellow precipitate (0.068 g, 79%). m.p. 58.0–59.1°C. IR (KBr): $\nu = 1676$s and 1662s ($(C{=}O)_{keto}$), 1626m (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.53$ (s, 1H, C(H)=N), 8.05–7.17 (14H, aromatic H), 3.85 (s, 2H, PCH_2, $^2J(PH) = 0$ Hz), 2.66 (t, 2H, CH_2, $^3J(HH) = 7$ Hz), 1.66 (m, 2H, CH_2CH_2), 1.31 (broad s, 18H, CH_2), 0.92 (t, 3H, CH_3, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 196.64$ (d, $C{=}O_{keto}$, $^2J(PC) = 8$ Hz), 157.89 (C=N), 141.67–120.88 (aromatic C's), 40.81 (d, PCH_2, $J(PC) = 22$ Hz), 35.50–14.12 (aliphatic C's). ^{31}P {H} NMR (toluene-C_6D_6): $\delta = -16.4$ (s). MS (E.I.), $m/z(\%) = 575$ (1.8) [M^+]. Anal. Found: C, 81.28; H, 8.13; N, 2.46. $C_{39}H_{46}NOP$ (575.79) calcd.: C, 81.36; H, 8.05; N, 2.43%.

3.13. cis-Bis(4'-diethylacetal-2-diphenylphosphino-acetophenonato-O,P) palladium(II) (10)

Compound **4** (0.406 g, 1.00 mmol) was allowed to react with $[Pd(acac)_2]$ (0.153 g, 0.50 mmol) in THF (35

ml). After stirring for 15 min, the solution was concentrated to *ca.* 10 ml and pentane (200 ml) was added, affording **10** as a yellow powder which was recrystallized from CH_2Cl_2/pentane (0.390 g, 85%). m.p. 210°C dec. IR (KBr): $\nu = 1526$ and 1496s cm^{-1} ((C–O) + (C=C)). ^1H NMR ($CDCl_3$): $\delta = 7.99–7.03$ (28H, aromatic H), 5.53 (s, 2H, $CH(OEt)_2$), 4.60 (d, 2H, PCH, $^2J(PH) = 1.9$ Hz), 3.55 (m, 8H, OCH_2), 1.22 (t, 12H, CH_3, $^3J(HH) = 7$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 183.03 (broad s, PCH=*C*(O)), 139.99–126.11 (aromatic C's), 101.30 (s, OCH), 78.61 (d, PCH, $J(PC) = 64$ Hz), 60.78 (s, OCH_2CH_3), 15.21 (s, OCH_2CH_3). $^{31}P\{^1H\}$ NMR (THF/C_6D_6): $\delta = 37.3$ (s). MS (FAB), $m/z(\%)$ = 917 (52) [$(M + H)^+$]. Anal. Found: C, 63.95; H, 5.49. $C_{50}H_{52}O_6P_2Pd \cdot 0.25\ CH_2Cl_2$ (917.33 + 21.33) calcd.: C, 64.19; H, 5.66%.

3.14. cis-Bis(4'-formyl-2-diphenylphosphino-acetophenonato-O,P)palladium(II) (11)

A suspension of silica gel (*ca.* 10 g) in 1,2-dichloroethane (35 ml) was treated under vigorous stirring with conc. H_2SO_4 (0.5 ml). Complex **10** (0.935 g, 1.02 mmol) was then added to this suspension. After 10 min, triethylamine (8 ml) was added in order to desorb the complex from the silica gel. The silica gel was filtered off and the yellow solution was concentrated to *ca.* 3 ml. Addition of pentane precipitated **11** as a yellow powder (0.635 g, 81%). m.p. 230°C dec. IR (KBr): $\nu = 1968$vs ($C{=}O_{ald}$), 1520s and 1488s ((C–O) + (C=C)) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 10.02$ (s, 2H, CH=O), 8.15–7.05 (28H, aromatic H), 4.75 (d, 2H, PCH, $^2J(PH) = 1.6$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 192.13$ (s, C(H)=O), 181.33 (t, COPd, $^2J(PC) \sim {}^3J(P'C) = 5$ Hz), 142.93–127.35 (aromatic C's), 81.30 (d, PCH, $J(PC) =$ 63 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 37.6$ (s). MS (FAB), $m/z(\%) = 769$ (70) [$(M + H)^+$]. Anal. Found: C, 65.33; H, 4.16. $C_{42}H_{32}O_4P_2Pd$ (769.08) calcd.: C, 65.59; H, 4.19%.

3.15. cis-Bis[2-diphenylphosphino-4'-{N-{4-[4'-(dodecyloxy)oxycarbonylphenyl]phenyl}methineimino}-acetophenonato-O,P]palladium(II) (12)

This complex was prepared using a procedure similar to that used for phosphine **6** but using amine H_2NA-12 and complex **11** (yield 87%). m.p. 184°C dec. IR (KBr): $\nu = 1722$m ($C{=}O_{ester}$), 1624w (C=N), 1510m and 1496m ((C–O) + (C=C)) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.50$ (s, 2H, CH=N), 8.18–6.95 (44H, aromatic H), 4.73 (broad s, 2H, PCH), 4.05 (t, 4H, OCH_2, $^3J(HH) =$ 6.5 Hz), 1.81 (m, 4H, OCH_2CH_2), 1.27 (broad s, 36H, CH_2), 0.89 (t, 6H, CH_3, $^3J(HH) = 6.5$ Hz). ^{13}C $\{^1H\}$ NMR ($CDCl_3$): $\delta = 182.39$ (broad s, COPd), 164.99*, 163.66*, 160.17 (s, C=N), 149.77–114.45 (aromatic C's), 80.03 (d, PCH, $J(PC) = 64.7$ Hz), 68.46 (OCH_2), 31.94–14.08 (aliphatic C's). ^{31}P $\{^1H\}$ NMR (C_6H_6/C_6D_6): $\delta = 37.5$ (s). MS (FAB), $m/z(\%) = 1527$ (1.3) [$(M + H)^+$)]. Anal. Found: C, 70.90; H, 6.34; N, 1.74. $C_{92}H_{98}N_2O_8P_2Pd \cdot 0.5CH_2Cl_2$ (1528.18 + 42.47) calcd.: C, 70.74; H, 6.35; N, 1.78%.

3.16. cis-Bis[2-diphenylphosphino-4'-{N-{4-[4'-(hexadecyloxy)oxycarbonylphenyl]phenyl}methineimino}-acetophenonato-O,P]palladium(II) (13)

This complex was prepared using a procedure similar to that used for phosphine **6** but using amine H_2NA-16 and complex **11** (yield 88%). m.p. 183°C dec. IR (KBr): $\nu = 1728$m ($C{=}O_{ester}$), 1624m (C=N), 1510m and 1496m ((C–O) + (C=C)) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.50$ (s, 2H, CH=N), 8.18–6.95 (44H, aromatic H), 4.74 (broad s, 2H, PCH), 4.05 (t, 4H, OCH_2, $^3J(HH) =$ 6.5 Hz), 1.81 (m, 4H, OCH_2CH_2), 1.27 (broad s, 52H, CH_2), 0.88 (t, 6H, CH_3, $^3J(HH) = 6.5$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 182.18$ (broad s, COPd), 164.96*, 163.58*, 160.19 (s, C=N), 149.68–114.33 (aromatic C's), 80.01 (d, PCH, $J(PC) = 63$ Hz), 68.36 (OCH_2), 31.92–14.10 (aliphatic C's). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 37.7$ (s). MS (FAB), $m/z(\%) = 1639$ (0.6) [$(M + H)^+$]. Anal. Found: C, 71.71; H, 6.92; N, 1.68. $C_{100}H_{114}N_2O_8P_2Pd \cdot 0.5CH_2Cl_2$ (1640.36 + 42.47) calcd.: C, 71.73; H, 6.89; N, 1.67%.

3.17. cis-Bis[2-diphenylphosphino-4'-{N-{4-[4'-(octadecyloxy)oxycarbonylphenyl]phenyl}methineimino}-acetophenonato-O,P]palladium(II) (14)

This complex was prepared using a procedure similar to that used for phosphine **6** but using the amine H_2NA-18 and complex **11** (yield 91%). m.p. 180°C (dec). IR (KBr): $\nu = 1728$s ($C{=}O_{ester}$), 1624m (C=N), 1510s and 1496s ((C–O) + (C=C)) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 8.50$ (s, 2H, CH=N), 8.18–6.95 (44H, aromatic's H), 4.73 (s, 2H, PCH, $^2J(PH) = 1.5$ Hz), 4.05 (t, 4H, OCH_2, $^3J(HH) = 6.5$ Hz), 1.81 (m, 4H, OCH_2CH_2), 1.27 (broad s, 60H, CH_2), 0.88 (t, 6H, CH_3, $^3J(HH) = 6.4$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta =$ 182.41 (t, COPd, $^2J(PC) \sim {}^3J(P'C) = 6$ Hz)), 164.98*, 163.66*, 160.17 (s, C=N), 149.80–114.45 (aromatic C's), 80.02 (d, PCH, $J(PC) = 64$ Hz), 68.47 (OCH_2), 31.98–14.08 (aliphatic C's). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 37.7$ (s). MS (FAB), $m/z(\%) = 1695$ (0.6) [$(M + H)^+$]. Anal. Found: C, 72.13; H, 7.30; N, 1.52. $C_{104}H_{122}N_2O_8P_2Pd \cdot 0.5CH_2Cl_2$ (1696.49 + 42.47) calcd.: C, 72.18; H, 7.13; N, 1.61%.

3.18. cis-Bis[2-Diphenylphosphino-4'-{N-[4-(dodecyl)-henyl]methineimino}-acetophenonato-O,P]palladium(II) (15)

This complex was prepared using a procedure similar to that used for phosphine **6** but using amine

H_2NA^*-12 and complex **11** (yield 90%). m.p. 150°C dec. IR (KBr): $\nu = 1626$s (C=N), 1520s and 1500vs ((C–O) + (C=C)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.49 (s, 2H, CH=N), 8.11–7.06 (36H, aromatic H), 4.72 (d, 2H, PCH, $^2J(PH) = 1.8$ Hz), 2.62 (t, 4H, $NC_6H_4CH_2$, $^3J(HH) = 7.6$ Hz), 1.63 (m, 4H, CH_2CH_2), 1.26 (broad s, 36H, CH_2), 0.88 (t, 6H, CH_3, $^3J(HH) = 6.8$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 182.01 (t, COPd, $^2J(PC) \sim {}^3J(P'C) = 5.5$ Hz), 159.23 (C=N), 149.60–120.78 (aromatic C's), 79.87 (d, PCH, $J(PC) = 63$ Hz), 35.46–14.07 (aliphatic C's). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 37.5$ (s). MS (FAB), $m/z(\%) = 1255$ (10) [$(M + H)^+$]. Anal. Found: C, 74.66; H, 7.13; N, 2.28. $C_{78}H_{90}N_2O_2P_2Pd$ (1255.95) calcd.: C, 74.59; H, 7.22; N, 2.23%.

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