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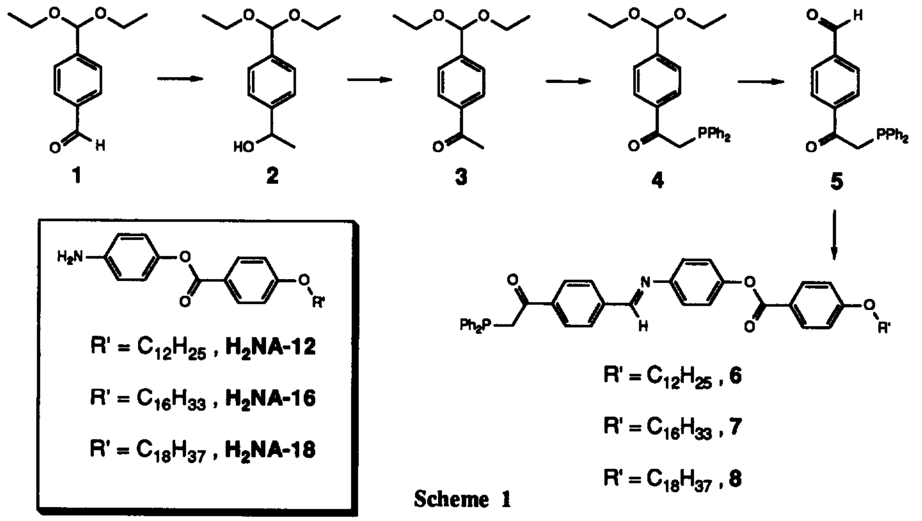
Synthesis and Coordination Properties of Novel Polyfunctional Phosphine Ligands

Daravong Soulivong, Dominique Matt* and Raymond Ziessel*
Ecole Européenne des Hautes Etudes des Industries Chimiques de Strasbourg
1, rue Blaise Pascal, F-67008 Strasbourg Cedex, France

Laurent Douce and Robert Deschenaux
Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland

Abstract: 4'-formyl-2-diphenylphosphino-acetophenone **5** has been prepared in four steps (50%) starting from terephtalaldehyde *mono*-(diethylacetal) **1**. Condensation of **5** with the *para*-substituted anilines H_2NA-i gives quantitatively the phosphine-imines **6-8**. Phosphines **4-6** instantaneously react with $Pd^{II}(acac)_2$ to yield the bis-enolato complexes *cis*-$[Pd^{II}\{[4'\text{-}(R)C_6H_4]C(O){=}CHPPh_2\}_2]$ ($R{=}CH(OC_2H_5)_2$, CH(O), CH=NA-12).

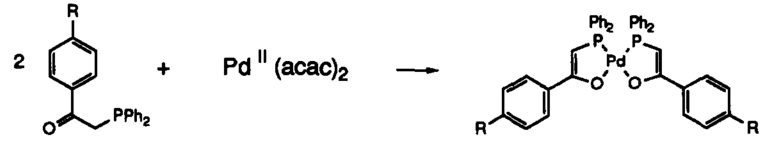
There is currently a growing interest for the design of multifunctional ligands allowing the synthesis of transition metal based molecular materials, *i.e.* molecules with multidimensional properties, such as metallomesogens[1] or complexes with non-linear optical (NLO) properties.[2] The occurence of such a property is usually achieved by subtle association of specific functionalities within a given ligand system. Useful subunits could be multipodal coordination centers, long chain substituents, donor/acceptor and/or paramagnetic groups. Despite the widespread use of P(III)-compounds in coordination chemistry, building blocks suitable for the synthesis of molecular materials very rarely contain tricoordinate phosphorus atoms.[3]



Scheme 1

We describe herein the stepwise synthesis and spectroscopic properties of three types of trifunctionalized phosphine ligands (Scheme 1). Their coordination properties toward palladium(II) were also investigated.

Reaction of **1** with CH_3MgBr gave [4-{$CH(OC_2H_5)_2$}C_6H_4]$CH(OH)CH_3$ **2** (67%). Oxidation of this secondary alcohol with MnO_2 led to the key ketone [4-{$CH(OC_2H_5)_2$}C_6H_4]$C(O)CH_3$ **3** (82%). Metallation of **3** with [$(CH_3)_3Si$]$_2$NLi and subsequent reaction with Ph_2PCl afforded the phosphine ligand [4-{$CH(OC_2H_5)_2$}C_6H_4]$C(O)CH_2PPh_2$ **4** which after deprotection of the aldehyde function gave [4-(CHO)C_6H_4]$C(O)CH_2PPh_2$ **5**. Condensation of **5** with the *para*-substituted anilines H_2NA-i [4,5] (azeotropic distillation in a Dean-Stark apparatus) gave the phosphine-imines [4-(CH=NA-i)C_6H_4]$C(O)CH_2PPh_2$ **6-8** (Scheme 1). All compounds were characterized by ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$-NMR, mass and infra-red spectroscopy, melting point and elemental analysis (see Table). The observed chemical shift values, δP, δ PCH_2 and δ PCH_2 are in good agreement with those reported for other β-keto phosphines;[6] the $^2J(PH)$ coupling constant is zero for all phosphines, and the $J(PC)$ coupling constants lie in the range 21-24 Hz. The novel trifunctionalized phosphine ligands **4**, **5** and **6** (2 equiv.) instantaneously react with $Pd^{II}(acac)_2$ to afford in yields > 80% the bis-enolato, *cis*-[Pd{[4'-(R)C_6H_4]C(O)=CHPPh$_2$}$_2$] complexes **9-11** respectively (Scheme 2).



R = $CH(OC_2H_5)_2$, **4** **9**
R = CHO , **5** **10**
R = $CH{=}NC_{12}H_{25}$, **6** **11**

Scheme 2

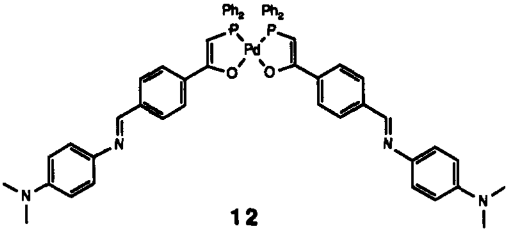
Deprotonation of the keto-phosphine occured during this reaction. The presence in the IR spectrum of strong bands at 1526-1510 and 1500-1494 cm^{-1} confirms the presence of an enolato-coordination type of the ligand. The *cis*-geometry is supported by the presence of a doublet for the PCH groups in the ^1H-NMR spectrum and a doublet in the $^{13}C\{^1H\}$ NMR spectrum for the corresponding carbon atoms.[7] This configuration has been observed in other square planar diphenylphosphino-enolato complexes.[8] Alternatively, complex **10** was synthesized in good yield (81%) by deprotection of complex **9** under acidic conditions adapting a literature procedure.[9] As checked by ^1H-NMR, condensation of **10** with H_2NA-12, under conditions similar to those described for the phosphine-imines **6-8**, gave quantitatively complex **11**.

Table : Selected data for compounds depicted in Schemes 1 and 2

Product	Isolated yield (%)	Melting point(°C)	^{1}H-NMR a) δPCH$_2$ ($^{2}J_{PH}$) or δPCH ($^{2}J_{PH}$)	^{13}C{^{1}H}-NMR δPCH$_2$ (J_{PC}) or δPCH (J_{PC}) b)	^{31}P{^{1}H}-NMR δP c)	MS d)
4	94	-	3.81(0)	40.25(21)	-17.1	406
5	95	103/4	3.83(0)	41.15(24)	-16.1	332
6	89	110/1	3.84(0)	40.98(22)	-16.0	711
7	89	109/10	3.84(0)	40.98(22)	-16.2	767
8	90	110/2	3.84(0)	40.98(22)	-16.3	796
9	85	210(dec)	4.60(1.9)	78.61(64)	+37.3	917(F)
10	93	230(dec)	4.75(1.6)	81.30(63)	+37.6	769(F)
11	92	184(dec)	4.73(br)	80.03(65)	+37.5	1527(F)
12	95	230(dec)	4.71(1.8)	79.58(63)	+37.7	1005(F)

a) Chemical shifts (ppm) are reported relative to residual protiated $CDCl_3$ (7.25).
b) Chemical shifts (ppm) are reported relative to the solvent $CDCl_3$ (77.0 ppm).
c) Chemical shifts (ppm) are reported relative to 85% H_3PO_4 and were measured in $CDCl_3$, except for **4** (in THF/C_6D_6).
d) Obtained by electron impact; corresponds to the molecular peak of the ligands (*m/e*); or by FAB$^+$(F) using *m*-nitrobenzylalcohol as matrix and correspond to [M+H]$^+$.

Complex **10** which contains two aldehyde functionalities is of particular interest for the preparation of highly polarized, neutral transition metal complexes. Indeed, reaction of **10** with two equiv. of N,N-dimethyl-1,4-phenylenediamine allows the straightforward synthesis of **12**. In this reaction, coordination of the enolato-phosphine and the *cis*-stereochemistry are maintained (see Table for characterizing data). Owing to the presence of the dimethylamino donor substituents and the acceptor character of the metal center, this type of complex may display substantial non-linear optical properties.[10]



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Further development of this work will be directed toward the modification: (i) of the P substituents as well as of the stereochemistry of the metal center in order to induce the formation of metallomesogens; (ii) of the R group notably by introduction of electron donating or withdrawing substituents to favour electronic communication.

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