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3,3',5,5' tetra(phosphaalkene) biphenyl: Synthesis of a Novel Bicyclometalating Bridging Ligand, and Structure of its Dipalladium Complex.

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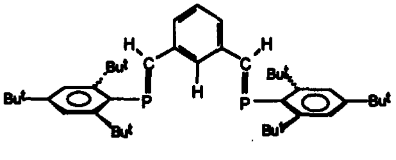
Abstract: A biphenyl derivative bearing four phosphaalkene groups in positions 3,3',5,5' has been synthesized and is shown to be a bis-terdentate chelating agent; this novel bridging ligand forms a complex with two palladium ions and the crystal structure of this dinuclear species has been obtained.

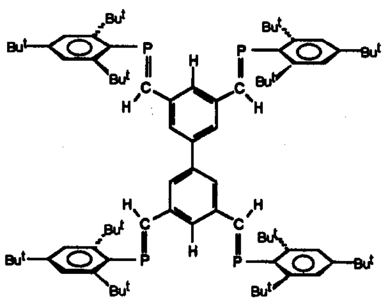
Due to the exceptional properties of binuclear metal complexes in electrochemistry and photochemistry [1], considerable efforts are currently made to synthesize new bridging ligands. In this context, nitrogen containing aromatic systems, like pyrazine [2] and bipyridine [3] are the most commonly used ligands and, very recently, Sauvage and coworkers [4] have described the synthesis of the bis-terdentate ligand tetrapyridinebiphenyl (*tpbp)* which can insure a particularly strong coupling between two metallic subunits.

In the present study, we have taken advantage of our previous synthesis [5] of a molecule containing a diphosphaalkene moiety, the di(tri-terbutyl phenylphosphaethylene)1,3-benzene, *dpeb-H*, to generate the novel bis-terdentate ligand 3,3',5,5' tetra(tri-*t*-butylphenyl phosphaethylene) biphenyl, *tpebp*-H_2, which is shown to form a complex with two palladium ions.

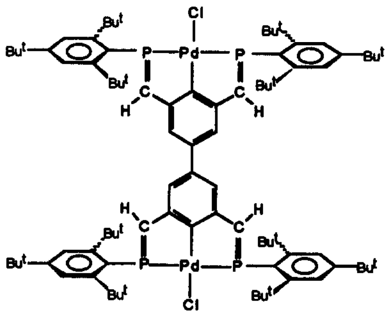


dpeb-H

Similarly to the *tpbp* ligand, the two metals are connected by the 4,4' biphenyl dianion but stabilization of the whole edifice is now insured by the four phosphaalkene moieties.



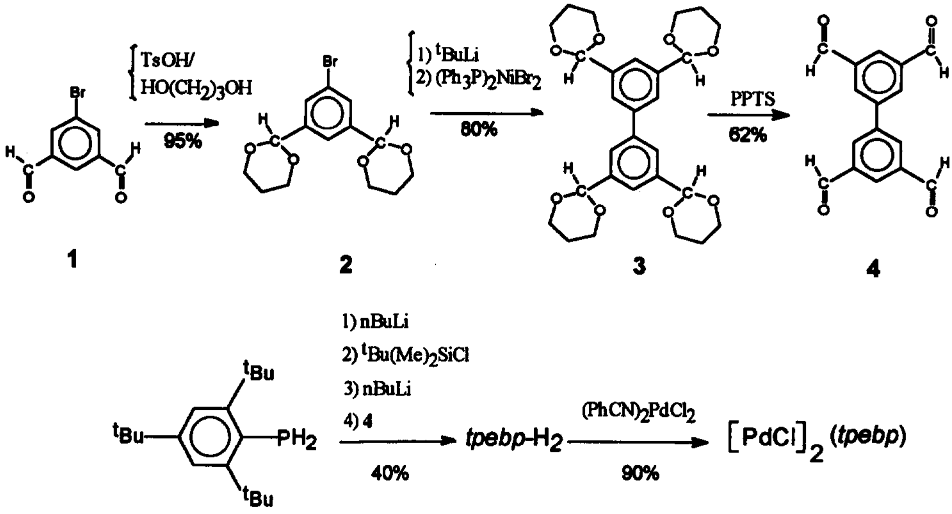
tpebp-H$_2$



(PdCl)$_2$ (tpebp)

The various steps of the synthesis of *tpebp-H$_2$* are shown in chart 1.

Chart 1.



5-bromoisophthalaldehyde (1) was obtained following the method recently published by Netzke and Snatzke [6]. Protection of the aldehyde functions of (1), using propane-1,3-diol with *p*-toluenesulfonic acid (TsOH) as catalyst, provided (2) (mp=82°C). (2) was then treated with ^{t}BuLi and condensation of the resulting lithio derivative in presence of $(Ph_3P)_2NiBr_2$ in THF afforded (3) (mp: 152-154°C). (4) was obtained after removal of the protecting groups in presence of pyridinium *p*-toluenesulfonate (PPTS) in a water/acetone mixture (4: mp>300°C).

tpebp-H$_2$ was obtained by following the same procedure as the one described for *dpeb-H* [5], but here, isophthalaldehyde was replaced by (4). After separation on a silical gel column with a hexane/CH_2Cl_2 mixture as an eluant, *tpebp-H*$_2$ was obtained as an oil which was recrystallized from an ether/CH_3CN mixture (mp=166-168°C).

The palladium complex was obtained as follows: $Pd(NCPh)_2Cl_2$ (41 mg) was added to a solution containing *tpebp-H*$_2$ (70 mg) in 3 ml of CH_2Cl_2. The mixture was stirred during 30 min. at room temperature, $[PdCl]_2$(*tpebp*) was recrystallized (orange crystals) from a CH_2Cl_2/EtOH mixture (3: mp>300°C).

All the compounds were characterized by ^1H and ^{31}P NMR spectroscopy.

The crystal structure [7] of $[PdCl]_2$ *(tpebp)* shows that the molecule is located on a two-fold axis passing through the central bond (Fig. 1). Each metal is coordinated to two phosphorus atoms and to an aromatic carbon atom. These three coordinating atoms, as well as the chlorine and palladium atoms are practically coplanar with the associated ring of the biphenyl moiety. This mean plane is almost perpendicular to the two tri *t*-butyl phenyl rings of the corresponding half-molecule. The torsion angle around the central C-C bond of the *tpebp* ligand is equal to 28.3° and is therefore expected to be small enough to allow communication between the two metal centers. The distance between the two Pd atoms is equal to 11.251(3) Å.

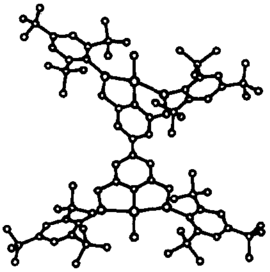


Figure 1.Crystal structure of $(PdCl)_2$(*tpebp*)

Acknowledgment
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7. ***Crystal data*** and structure refinement for $[PdCl]_2$ *(tpebp)*. Cell parameters and reflection intensities were measured at room temperature on a STOE STADI 4 diffractometer with Mo-Kα radiation (λ = 0.71069 Å). $(C_{44}H_{62}P_2PdCl)_2$ $(C_2H_5OH)_{0.5}$, M =1635.6, monoclinic, space group $I2/a$,a = 21.026(3), b = 22.080(4), c = 22.994(4) Å,V = 9637(3) Å^3, Z = 4, Dx = 1.13(Mg.m^{-3}), μ = 0.527 mm^{-1}, F(000) = 3456. Data collection: -20< h <20, 0< k <21, 0< l <22 ; ω-2θ scans, absorption corrections [8]: A*min. = 1.044, A*max.= 1.199. Of the 4560 unique reflections, 2509 were considered as observed [$|Fo| > 4\sigma(F0)$] and used in structure refinement. The structure was solved by direct methods (MULTAN 87) [9] and refined by full matrix least-squares with the XTAL 3.2 program [10]. Atomic scattering factors and anomalous-dispersion terms are taken from ref. 11. The maximum and minimum residual electron densities in the final ΔF map were 0.89 and -1.31 eÅ^{-3} respectively. Final R factors are: R = wR = 0.078 (w=1) . A disordered solvent molecule has been located around a two-fold axis and 3 atomic sites refined with a population of 0.25. Atomic coordinates, bond lengths and angles, and atomic displacement parameters have been deposited with the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England.
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