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Ab initio Study of New Phosphino PCP Pincer Ligand, $\{C_6H_4\text{-}1\text{-}(CH_2PPh_2)\text{-}3\text{-}(CH(CH_3)PPh_2)\}$

ALI NAGHIPOOR*, ZAHRA HAJI GHASEMI† and SHAHRYAR ABBASI
Department of Chemistry, Faculty of Science, University of Ilam, Ilam 69315, Iran
E-mail: naghipour51@yahoo.com

Multidentate ligand systems, both cyclic and acyclic can be designed to bind transition metals in a predictable manner. The steric constraints of such ligands and the nature of the donor atoms determine to a large extent the stability and properties of the metal complexes. Here in, the new PCP pincer ligand, $\{C_6H_4\text{-}1\text{-}(CH_2PPh_2)\text{-}3\text{-}(CH(CH_3)PPh_2)\}$, has been theoretically studied by *ab initio* restricted Hartree-Fock (RHF).

Key Words: *Ab initio* study, Phosphino PCP pincer ligand.

INTRODUCTION

The chemistry of pincer ligands and their palladium and platinum complexes is a fascinating and active area of research for both experimentalists and theoreticians[1-8]. Among pincer ligands, PCP pincers and in pincer complexes, the palladium PCP pincer complexes are more important due to their stability and catalytic activity in organic synthesis. Much of the research on PCP pincer complexes has focused on complexes of diphosphinoxylenes: $\{C_6H_4\text{-}1,3\text{-}(CH_2PR_2)_2\}$. Modifications of the benzylic positions and phosphino R groups have been used to "tune", the steric, electronic and stereochemical properties of these ligands thus their metal complexes[9-13].

CALCULATIONAL METHODS

Based on our knowledge it is clear that the inclusion of a relativistic effect is essential for heavy-metal complexes, such as second and third row transition metals. Effective core potentials (ECPs) can be used in conventional *ab initio* methods and in density functional theory and both methods are most important tools for theoretical calculations of transition metal complexes. Scalar relativistic effects, which replace the chemically inert core electrons by means of a set of parameterized functions that are derived from relativistic calculations, have been included in relativistic ECPs. In addition, the electron correlation effect is considered in the DFT method itself. In the present work, the geometries of the palladium complexes were fully optimized at the restricted Hartree-Fock (RHF)[14] levels of theory using the

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†Department of Chemistry, Azad University of Ilam, Ilam, Iran.

GAUSSIAN 98 program[15] on a notebook computer with a 1.73 GHz processor and 1 GHz RAM. The *ab initio* calculations of the PCP pincer ligand, $\{C_6H_4\text{-1-}(CH_2PPh_2)\text{-3-}(CH(CH_3)PPh_2)\}$ have been carried out (Fig. 1). All the calculations have been calculated using the standard LanL2MB basis set theory using a suite of GAUSSIAN 98 programs[16].

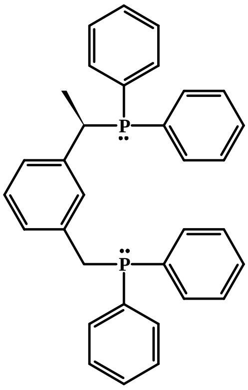

Fig. 1. Structure of PCP pincer ligand, $\{C_6H_4\text{-1-}(CH_2PPh_2)\text{-3-}(CH(CH_3)PPh_2)\}$

The details of the structure determination including selected bond lengths and angles are listed in Table-1.

TABLE-1
SELECTED THEORETICAL BOND LENGTHS (Å) AND BOND ANGLES (°) OF THE CALCULATED STRUCTURE USING LanL2MB BASIS SET

Bond lengths	Å	Bond angles	°
P(14)-C(22)	1.8581	P(14)-C(22)-C(33)	120.0806
P(14)-C(21)	1.8590	P(14)-C(22)-C(32)	120.5427
P(13)-C(20)	1.8606	C(31)-C(21)-P(14)	120.1765
P(13)-C(19)	1.8596	C(30)-C(21)-P(14)	120.5638
C(11)-P(14)	1.8941	P(13)-C(20)-C(29)	120.3676
C(10)-P(13)	1.9003	P(13)-C(20)-C(28)	120.3981
		P(13)-C(19)-C(27)	121.1548
		P(13)-C(19)-C(26)	119.7564
		C(11)-P(14)-C(21)	119.5562
		C(11)-P(14)-C(22)	119.5540
		C(22)-P(14)-C(21)	120.8310
		C(10)-P(13)-C(19)	120.1289
		C(10)-P(13)-C(20)	118.6433
		C(20)-P(13)-C(19)	118.9918
		P(14)-C(11)-H(17)	108.6060
		P(14)-C(11)-H(18)	109.2742
		C(5)-C(11)-P(14)	110.7487
		C(12)-C(10)-P(13)	112.8124
		P(13)-C(10)-H(16)	106.7845
		C(6)-C(10)-P(13)	109.7860

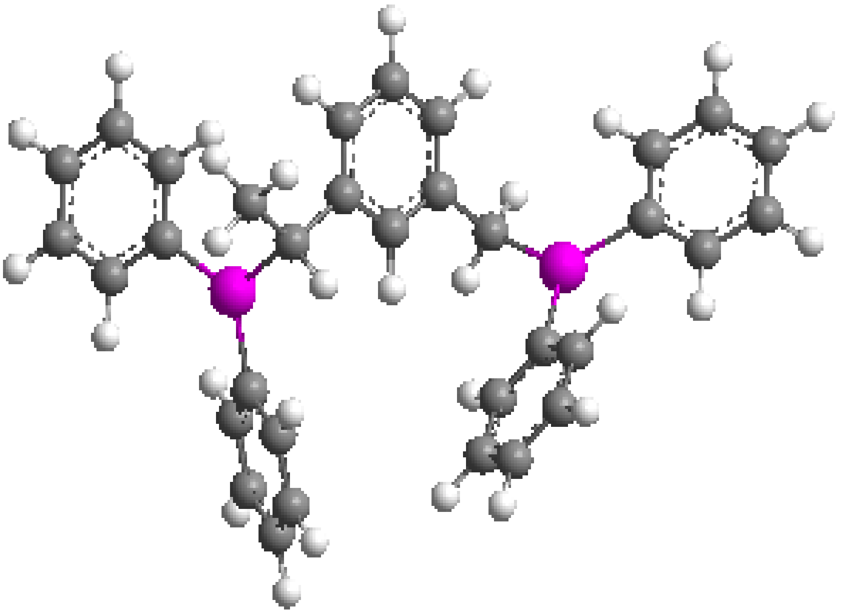

Fig. 2. The obtained structure of the PCP pincer ligand, {C_6H_4-1-(CH_2PPh_2)-3-($CH(CH_3)PPh_2$)} using the LanL2MB basis set

RESULTS AND DISCUSSION

The structure of the ligand shows the ability of connection to, metal like palladium or platinum as tridentate PCP pincer ligand in toluene solvent under nitrogen at 120 °C or it can be connected to metal like palladium, platinum, nickel and others as a bidentate ligand in a same solvent at low temperature[17-20]. The occurrence of one methyl group on carbon number 3 - ($CH(CH_3)PPh_2$ make this ligand as a chiral ligand for special catalytic reaction to act as enantiomer selective reaction and base on the biphenyl group on each side of the ligand make it as a strong catalyst, more active and more stable in C-C coupling reaction including aryl chloride on Heck reaction[3-6,13,17-23].

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