Journal of Organometallic Chemistry 772-773 (2014) 314–319

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis and structures of molybdenum complexes of aryl- and alkylphosphonium triphenylcyclopentadienylide ligands

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ARTICLE INFO

Article history:
Received 15 April 2014
Received in revised form
30 August 2014
Accepted 5 September 2014
Available online 18 September 2014

Keywords:
Molybdenum coordination complexes
Phosphonium cyclopentadienylide
Cyclopentadiene
Pyrylium salts

ABSTRACT

The hitherto new molybdenum coordination complexes (η^5-$C_5HPh_3PEt_3$)$Mo(CO)_3$ (**I**), (η^5-$C_5HPh_3PMe_2Ph$)$Mo(CO)_3$ (**II**) and (η^5-$C_5HPh_3PMePh_2$) $Mo(CO)_3$ (**III**) has been synthesized and characterized *via* substitution reactions of triethylphosphonium triphenylcyclopentadienylide ($C_5HPh_3PEt_3$), dimethylphenylphosphonium triphenylcyclopentadienylide ($C_5HPh_3PMe_2Ph$) and diphenylmethylphosphonium triphenylcyclopentadienylide ($C_5HPh_3PMePh_2$) with $Mo(CO)_3(CH_3CN)_3$ respectively as a stable coordination complexes. The structure of compound was characterized on the basis of ^1H NMR, ^{13}C NMR, ^{31}P NMR spectroscopies, elemental analyses, and X-ray crystallography. The structures of the free ligands and their molybdenum complexes **I**, **II**, and **III** were compared with the reported analogous compound ($C_5H_4PMePh_2$) and its complex (η^5-$C_5H_4PMePh_2$)$Mo(CO)_3$. The IR spectrum of complex in which values of ν(CO) and the M–C_5 (centroid) bond lengths showing strong evidences about the effects the electron-donating ability of ligands towards $Mo(CO)_3(CH_3CN)_3$ by the multiple phenyl group of cyclopentadienyl ring. The P–C (1) bond distance of **II** shorter than that of **III** indicated that the steric effect of PR_3 moiety is the dominating factor.

Introduction

Phosphonium cyclopentadienylide (PCPY) ligands and their coordination complexes is currently important and attractive area of research because of their potential applications in the large range of disciplines including organometallic chemistry and catalytic field [1]. $C_5H_4PPh_3$ has been published in past over two decades [2–6]. Recently, Browinie et al. has reported a new ligand $C_5H_4PMePh_2$, its coordination chemistry [7]. Also proposed coordinating and catalytic behavior of the PCPY ligands related to the substituents on phosphorus [8]. Now a days scientist facing the challenges in this research field due to the limited sources of reported articles. Difficulties in synthetic method and it characterization induces of PCPYs, Steric and electronic factors in co-ordination chemistry of PCPYs and effects of the substituents of ligand on metal complex is largely unexplored.

Recently, we have reported a facile route to synthesize new arylphosphonium triphenylcyclopentadienylide and alkylphosphonium triphenylcyclopentadienylide ligands by intramolecular Wittig reaction of α,α′-monosubstituted 2,4,5-triphenylpyrylium salt and η^3-phosphines [9]. It provides important knowledge to investigate the effects of ligand substitution on metal complex structures, including substituents on cyclopentadienyl ring and phosphorus.

Herein we report the synthesis of new molybdenum complexes of ligands $C_5HPh_3PEt_3$, $C_5HPh_3PMe_2Ph$ and $C_5HPh_3PMePh_2$. And in addition demonstrate the structural comparisons with those reported analogous compounds such as $C_5H_4PPh_3$ and $C_5H_4PMePh_2$. All structures of ligands shown in Scheme 1.

Experimental section

All reactions were carried out under the argon atmosphere, Ligands $C_5HPh_3PEt_3$, $C_5HPh_3PMe_2Ph$ and $C_5HPh_3PMePh_2$ were synthesized by using our previously reported method [9]. $Mo(CO)_3(CH_3CN)_3$ was synthesized according to the literature [10].

NMR spectra were recorded using INOVA spectrometer at 400 MHz. All ^1H and ^{13}C NMR spectra were referenced to carbons or residual protons present in the deuterated solvents with respect to TMS at δ 0. ^{31}P NMR was referenced to external 85% H_3PO_4. X-ray crystal structure determinations were performed on a Bruker SMART APEX CCD diffractometer with graphite-monochromated

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http://dx.doi.org/10.1016/j.jorganchem.2014.09.006
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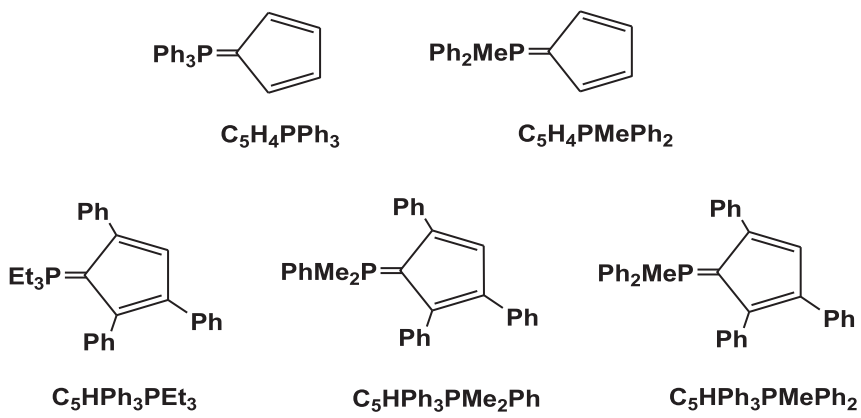

Scheme 1. Structures of $C_5H_4PPh_3$, $C_5H_4PMePh_2$, $C_5HPh_3PEt_3$, $C_5HPh_3PMe_2Ph$ and $C_5HPh_3PMePh_2$.

Mo-Kα ($\lambda = 0.71073$ Å) using the SMART and SAINT programs. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1. All non-hydrogen atoms were refined anistropically.

*Synthesis of (η^5-$C_5HPh_3PEt_3$)Mo(CO)$_3$ (**I**)*

In 20 mL of THF, a reaction mixture of ligand $C_5HPh_3PEt_3$ 0.41 g (1.0×10^{-3} mol) and $Mo(CO)_3(CH_3CN)_3$ 1.06 g (3.5×10^{-3} mol) was refluxed under the argon for 3 h. Then the reaction mixture was cooled and filtered, and the solid residue was washed with 20 mL of THF. The resulting filtrate was then treated with 200 mL of hexanes formed yellow precipitate, which collected and washed with 30 mL hexanes. The solid was dried in vacuum; yield about 0.34 g (57%) of yellow product, Produced single crystal by diffusion method of crystallization by using methylene chloride and hexane as solvent.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 7.60–7.03 (15H, m, Ph), 5.72 (1H, d, $^4J_{P-H} = 4.0$ Hz, PCPhC*H*), 1.78–1.69 (6H, m, P(C*H*$_2$CH$_3$)$_3$), 1.08–1.00 (9H, m, P(CH$_2$C*H*$_3$)$_3$). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ: 232.1, 134.8, 134.1, 132.5, 130.5, 129.6, 129.2, 128.9, 128.6, 128.1, 127.7, 127.0, 123.4, 119.6, 117.9, 113.8, 96.5, 71.6, 17.6, 7.5. ^{31}P NMR (CD_2Cl_2, 100 MHz) δ: 33.00. Anal. Calcd for $C_{32}H_{31}MoO_3P$: C, 64.85; H, 5.24. Found: C, 64.54; H, 5.31. IR (CH_2Cl_2): 1929, 1836 cm^{-1}.

*Synthesis of (η^5-$C_5HPh_3PMe_2Ph$)Mo(CO)$_3$ (**II**)*

The compound (η^5-$C_5HPh_3PMe_2Ph$)Mo(CO)$_3$ (**II**) was synthesized and characterized as (**I**) with the using of ligand $C_5HPh_3PMe_2Ph$ 0.43 g (1.0×10^{-3} mol) and $Mo(CO)_3(CH_3CN)_3$ 1.06 g (3.5×10^{-3} mol).

^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 7.79–7.12 (20H, m, Ph), 5.87 (1H, d, $^4J_{P-H} = 4.0$ Hz, PCCPhC*H*), 1.84 (3H, d, $^2J_{P-H} = 12.0$ Hz, Me), 1.75 (3H, d, $^2J_{P-H} = 16.0$ Hz, Me). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ: 233.1, 135.0, 134.3, 134.1, 134.0, 133.8, 133.2, 132.5, 129.7, 129.6, 129.4, 128.1, 127.9, 127.0, 124.2, 123.8, 123.3, 122.9, 121.4, 112.3, 95.6, 75.3, 16.3. ^{31}P NMR (CD_2Cl_2, 100 MHz) δ: 13.88. Anal. Calcd for $C_{34}H_{27}MoO_3P$: C, 66.66; H, 4.41. Found: C, 65.99; H, 4.52. IR (CH_2Cl_2): 19,134, 1845 cm^{-1}.

*Synthesis of (η^5-$C_5HPh_3PMePh_2$)Mo(CO)$_3$ (**III**)*

The compound (η^5-$C_5HPh_3PMePh_2$)Mo(CO)$_3$ (**III**) was prepared and characterized as (**I**) and (**II**). Ligand $C_5HPh_3PMePh_2$ 0.49 g (1.0×10^{-3} mol) and $Mo(CO)_3(CH_3CN)_3$ 1.06 g (3.5×10^{-3} mol). ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 7.62–6.89 (25H, m, Ph), 5.83 (1H, d, $^4J_{P-H} = 4.0$ Hz, PCCPhC*H*), 1.92 (3H, d, $^2J_{P-H} = 12.0$ Hz, Me). ^{13}C NMR (CD_2Cl_2, 100 MHz) δ: 229.4, 134.4, 133.6, 133.3, 131.7, 131.4, 131.3, 130.4, 129.6, 129.5, 129.4, 129.3, 128.3, 128.2, 128.1, 127.7, 127.6, 126.7, 126.3, 125.4, 120.0, 119.9, 118.8, 113.6, 95.3, 71.3, 15.9. ^{31}P NMR (CD_2Cl_2, 100 MHz) δ: 18.06. Anal. Calcd for $C_{39}H_{29}MoO_3P$: C, 69.43; H, 4.30. Found: C, 68.97; H, 4.48. IR (CH_2Cl_2): 1936, 1848 cm^{-1}.

Results and discussion

Synthesis, structure, and spectroscopic properties of $C_5HPh_3PEt_3$, $C_5HPh_3PMe_2Ph$ and $C_5HPh_3PMePh_2$

Ligands $C_5HPh_3PEt_3$, $C_5HPh_3PMe_2Ph$ and $C_5HPh_3PMePh_2$ were synthesized by intramolecular Wittig reaction of α,α'-mono-substituted 2,4,5-triphenylpyrylium salt and η^3-phosphines. We have characterized these ligands by ^{1}H NMR, ^{31}P NMR, ^{13}C NMR spectroscopy, elemental analyses, and produced X-ray-quality single crystals of $C_5H_4PMePh_2$ were obtained (Fig. 1), and the primary investigation indicates that its electronic structure is similar to $C_5H_4PPh_3$ and $C_5H_4PMePh_2$ [9]. Here we would perform the further investigation and make the direct comparisons of the coordination chemistry of $C_5H_4PPh_3$, $C_5H_4PMePh_2$ and $C_5HPh_3PMe_2Ph$. To facilitate comparisons, we employ a uniform labeling scheme and the atom numbering for the carbon and hydrogen atoms of the

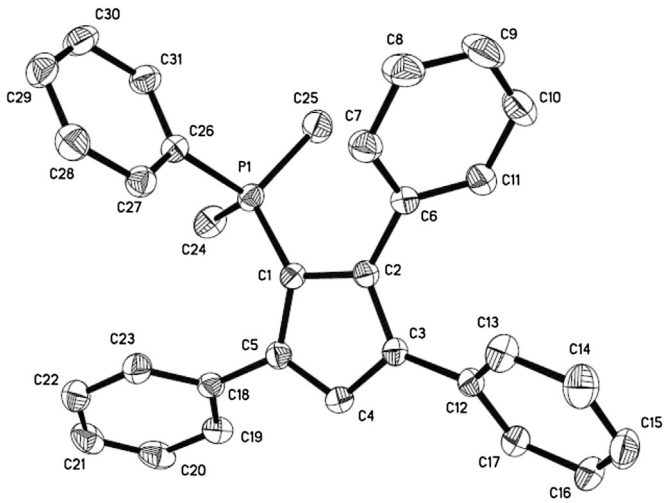

Fig. 1. Molecular structure of ligand $C_5HPh_3PMe_2Ph$.