Molybdenum and tungsten complexes with bis(diphenylphosphinoamine) ligands: synthesis, characterization and their catalytic activity towards ethylene oligomerization

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ABSTRACT

The bis(diphenylphosphino)amine ligands [Ph₂PN(R)PPh₂ = PNP; R = cyclohexyl (Cy) (1a), phenyl (Ph) (1b), benzyl (Bz) (1c)] have been synthesized. They were reacted with M(CO)₃(MeCN)₃ (M = Mo, W) in THF to yield the corresponding mononuclear complexes M(CO)₄(PNP). The solid state structures of the Mo complex of 1b and the W complex of 1b and 1c has been established by X-ray crystallography. The seven-coordinate iodide complexes of 1a and 1c were also synthesized and characterized by ¹H and ³¹P NMR. The Mo tetracarbonyl complexes of the ligands 1a and 1c were screened for activity towards ethylene oligomerization in the presence of MAO in toluene. However, both complexes only showed limited activity towards ethylene oligomerization.

INTRODUCTION

Diphosphinoamine ligands of the type X₂PN(R)PX₂ have attracted much interest and their chemistry has been well studied, with several papers published on the subject in the last few decades. These ligands possess two chemically distinct donor sites (two soft P donors and one hard N donor atom) that are each able to interact to a different extent with the metal centre and this may help to stabilize intermediate oxidation states or geometries during a catalytic cycle. Another attractive feature of these ligands is that their electronic and steric factors can also be altered in a systematic way by varying the substituents on phosphorus and nitrogen centers, thus their widespread use in transition metal chemistry and catalysis, most notably for the selective trimerization and tetramerization of ethylene.

Driven by the need for linear alpha-olefins (LAOs) in the chemical industry, much attention has been devoted to the development of ethylene oligomerization catalysts capable of selectively producing 1-hexene and 1-octene, which are mainly used as co-monomers in the production of linear low-density polyethylene (LLDPE). For example, Cr(III) complexes supported by PNP ligands, which have emerged in the recent years, have been proven to be highly active catalysts for
this purpose. The latest mechanistic studies show that the catalytic cycle proceeds through metallocycle intermediates, which gives the catalyst high selectivities towards LAOs.

By contrast, the catalytic activity of the other group VI metals molybdenum and tungsten towards ethylene oligomerization has remained unexplored although several molybdenum complexes of PNP ligands have been reported in the literature. Small differences in these ligands have been shown to cause significant changes in their coordination behavior and the structural features of the resulting complexes. The PNP ligands are known to coordinate to Mo and W centers in monodentate, chelating or bridging modes (See Fig. 1).

![Fig. 1. Binding modes of PNP ligands to Mo and W. (a) monodentate, (b) cis-chelating and (c) bridging.](image)

In this report, the syntheses and characterization of the Mo(0) and W(0) complexes of the bis(diphenylphosphino)amine ligands [Ph2PN(R)PPh2 = PNP; R = Cy (1a), Ph (1b), Bz (1c)] is described, and the activity of a few selected complexes towards ethylene oligomerization is also investigated. Currently, not many Mo and W complexes of bis(diphenylphosphino)amine ligands have been synthesized, of which two have been crystallographically characterized. These are cis-[Mo(CO)4{Ph2PN(o-C6H4OMe)PPh2}]6 and cis-[W(CO)4{Ph2PN('Pr)PPh2}]7. The syntheses and characterization of the Mo(II) iodide complexes of ligands 1a and 1c, [MoI2(CO)3(Ph2PN(Cy)PPh2)] (4a) and [MoI2(CO)3(Ph2PN(Bz)PPh2)] (4b), are also reported.

RESULTS AND DISCUSSION

**Synthesis of PNP Ligands**

\[
\text{RNH}_2 + 2\text{PPh}_2\text{Cl} + \text{Et}_3\text{N} \rightarrow \text{Ph}_2\text{PN(R)PPh}_2 \quad \text{R = Cy (1a), Ph (1b), Bz (1c)}
\]

The PNP ligands (1a-c) were synthesized by the addition of the appropriate primary amine to diphenylphosphinechloride PPh2Cl in a 1:2 stoichiometric ratio, which react in an acid condensation reaction to yield the desired PNP ligands in moderate to good yields (40-75%). The ligands were characterized by \(^1\)H and \(^{31}\)P NMR. The spectroscopic data are in accordance with the literature data.

**Synthesis of M(CO)\(_4\)(PNP) Complexes**
Reaction of the tris(acetonitrile) precursors M(CO)₃(MeCN)₃ with the respective PNP ligands in THF at 40 °C for 48 hr afforded the corresponding molybdenum and tungsten complexes 2a-c and 3a-c (Scheme 1), which were isolated as yellow solids in moderate to good yields (36-70%). The complexes 2b, 3b and 3c have been further characterized by X-ray crystallography.

Scheme 1. Synthetic route to 2a-c and 3a-c

The iodide complexes were synthesized in an attempt to oxidize the molybdenum metal center from an oxidation state of 0 to +2. The tris(acetonitrile) precursor Mo(CO)₃(MeCN)₃ was first reacted with I₂ in MeCN at 0 °C, after which the solvent was removed under vacuo.

Scheme 2. Synthetic route to complexes 4a and 4b.

The ethylene oligomerization behavior of complexes 2a and 2c were evaluated in toluene with MAO activation. A catalytic mixture containing the PNP complex:MAO (1:1000) was mixed under 25 bar pressure of ethylene at 50 °C in toluene in the Endeavor Parallel Reactor for 30 min. The results are summarized in Table 4. Also included are the data of a few other Mo and W complexes for comparison.

Table 4. Ethylene oligomerization data for complexes 2a and 2c.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Productivity (g&lt;sub&gt;product&lt;/sub&gt;/g&lt;sub&gt;M&lt;/sub&gt;)</th>
<th>Product Distribution (%)</th>
<th>1-C₄ in C₄ (%)</th>
<th>1-C₆ in C₆ (%)</th>
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<tr>
<td>1</td>
<td>Mo(CO)₄{PPh₂PN(Cy)PPh₂}</td>
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<td></td>
<td>Formula</td>
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<td>71.2</td>
<td>28.8</td>
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<td>----</td>
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<td>------</td>
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<td>------</td>
</tr>
<tr>
<td>2</td>
<td>Mo(CO)$_4$[PPh$_2$PN(Bz)PPh$_2$]</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Mo(CO)$_4$[PPh$_2$PN(CH$_2$CH$_2$CH$_2$OCH$_3$)PPh$_2$]</td>
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<tr>
<td>4</td>
<td>Mo(CO)$_4$[PPh$_2$PN(CH$_2$CH$_2$CH$_2$SCH$_3$)PPh$_2$]</td>
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<td>0</td>
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<tr>
<td>5</td>
<td>W(CO)$_4$[PPh$_2$PN(CH$_2$CH$_2$CH$_2$SCH$_3$)PPh$_2$]</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
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*a* Unpublished data.

**ACKNOWLEDGEMENTS**

I would like to thank my supervisor, Dr. Zhao Jin, for giving me the opportunity to work on this project, and my graduate student mentor, Ms. Li Shenyu for her patience and guidance.

**REFERENCES**


