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NH-functionalized tungsten complexes of 2-(dimethylphosphino)imidazole

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Abstract

Ligand substitution in $W(CO)_4(NO)(ClAlCl_3)$ with 2-(dimethylphosphino)imidazole (dmpi) bearing an acidic NH functionality afforded W(Cl)(CO)(NO)(bdmpi)(dmpi) (**1**) (bdmpi = 1,2-bis(dimethyl-phosphino)imidazole), while the reaction of dmpi with $W(Cl)(NO)(P(OMe)_3)_4$ led to the isolation of $W(Cl)(NO)(dmpi)_4$ (**2**) together with $W(Cl)(NO)(bdmpi)(dmpi)_2$ (**3**). Attempts to replace the chloride by a hydride ligand in **1**–**3** applying various hydride reagents did not lead to stable products. The soluble compound $W(Cl)(NO)(dmpe)(dmpi)_2$ (**5**) was prepared by an alternative route from $W(Cl)(NO)[P(OMe)_3)]_4$ via the intermediacy of $W(Cl)(NO)(P(OMe)_3)_2(dmpe)$ (**4**). The protection of the NH function in **5** was approached applying BuLi and subsequently Me_3SiCl to afford $[W(Cl)(NO)(dmpe)(tmsdmpi)_2]$ (tmsdmpi = 1-trimethylsilyl-2-dimethylphosphino-imidazole) (**6**) which could not be isolated in pure form. The reaction of **5** with $NaHBEt_3$ led to the formation of a deprotonated and nitrogen-coordinated salt Na[W(NO)(dmpe)(dmpi)(tebdmpi)] (**7**) (tebdmpi = 2-dimethylphosphino-3-triethylboro-imidazole). Compound **7** crystallized from CH_3CN to establish a one-dimensional chain structure in the solid state. The structures of compounds **1**–**5** and **7** were studied by single-crystal X-ray diffraction.

Keywords: Tungsten; Nitrosyl; Dimethylphosphinoimidazole; Crystal structure

1. Introduction

Catalytic hydrogenations play a pivotal role in homogeneous catalysis. Recently, major research efforts were devoted to the development of catalytic ionic hydrogenations using H^+ and H^- as a H_2 equivalent. One sub-class of this latter type of reaction follows a concerted mechanism [1–4], where the hydride and proton transfer to the unsaturated substrate occur more or less simultaneously requiring, in addition, the hydride and proton sources to be arranged in close spatial vicinity. The hydrogenation of organic carbonyl compounds could thus take place in the secondary coordination sphere of complexes and would not require a vacant site, which middle transition elements like tungsten normally cannot easily provide. The design of efficient such bifunctional hydrogenation catalysts or precatalysts would, however, demand a transition metal hydride of appropriate hydridicity and ligands with an acidic function, for instance, coordinated or noncoordinated NH or OH groups [2–8,6,9,10]. The coordinated forms of such moieties usually possess increased acidities with the possibility of facile deprotonation. In this paper, we intended to approach the preparation of complexes with acidic ligands of the non-ligating NH type and it seemed appropriate to build these functionalities into strongly cis-σ-donating phosphines, the latter to enhance hydridicity of the M–H bond [11–16]. We therefore approached the preparation of 2-(dimethylphosphino)imidazole (dmpi) to apply this ligand in tungsten nitrosyl complexes.

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2. Results and discussion

2.1. Preparation of 2-(dimethylphosphino)imidazole (dmpi)

Starting from *N*-(diethoxymethyl)imidazole dmpi was prepared by a route analogous to that of tris(4,5-dimethylimidazol-2-yl)phosphine [17]. The reaction of Me_2PCl with the lithium salt of *N*-(diethoxymethyl)imidazole gave the N-protected 2-(dimethylphosphino)imidazole (Scheme 1). The latter characterized through NMR spectroscopy including ^1H, ^{31}P, ^{13}C NMR, NOESY, ^1H-COSY and ^{13}C–^1H correlation spectra. Deprotection of the *N*-functionalized group was effected by dissolution in 10:1 acetone–water and heating to 50 °C for 8 h. A too large excess of water reduced the yield of dmpi greatly. The crude mixture was purified by recrystallization from dry CH_2Cl_2 to give dmpi as white needles in a yield of 75% based on *N*-(diethoxymethyl)imidazole. dmpi was fully characterized by IR, NMR, elemental analysis, MS and a single crystal X-ray analysis. The ^{31}P NMR spectrum of dmpi in CD_2Cl_2 reveals a singlet at −58.7 ppm and its ^1H NMR spectrum displays a broad resonance at 11.31 ppm characteristic for the NH function. Its structure revealed a pyramidal geometry at the phosphorus atom.

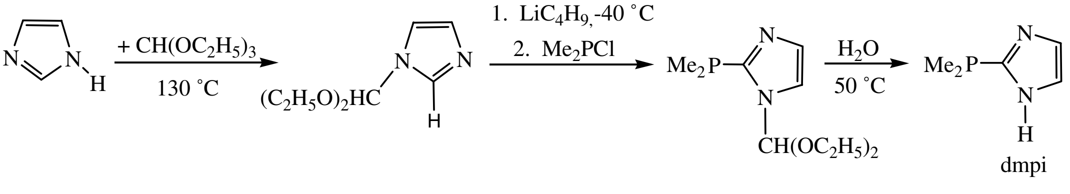
2.2. Reactions of dmpi with tungsten nitrosyl complexes

The reaction of $W(NO)(CO)_4(ClAlCl_3)$ [18] with a 6-fold excess of dmpi in THF at 85 °C for 6 d gave W(Cl)(CO)(NO)(dmpi)(bdmpi) (**1**) (bdmpi = 1,2-bis(dimethylphosphino)imidazole) in 71% yield (Scheme 2), which was characterized by IR, NMR, elemental analysis and single crystal X-ray diffraction.

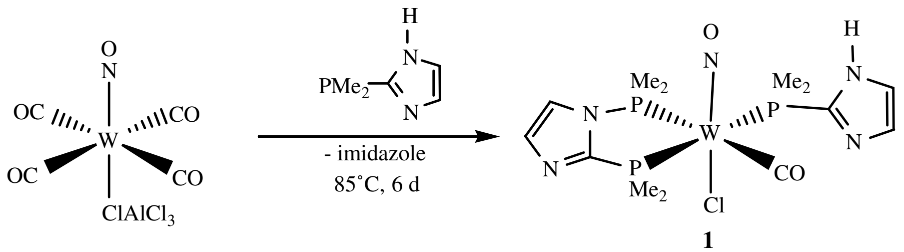
In **1**, a new ligand 1,2-bis(dimethylphosphino)imidazole (bdmpi) was generated bearing a new P–N bond. It is suggested that **1** was produced via an intermediacy of $[W(Cl)(CO)(NO)(dmpi)_3]$ in which two neighbouring dmpi ligands underwent an imidazole disproportionation forming a coordinated bdmpi ligand and a free imidazole molecule.

The IR spectrum of **1** showed *ν*(CO) and *ν*(NO) bands at 1952 and 1599 cm^{-1}, which confirmed the presence of both types of ligands. The ^{31}P NMR spectrum in $CDCl_3$ displayed three groups of doublet of doublet resonances with satellites at 82.7 ppm ($^2J_{PP\text{-}trans} = 159$ Hz, $^2J_{PP\text{-}cis} = 25$ Hz, $^1J_{PW} = 463$ Hz), −11.5 ppm ($^2J_{PP\text{-}cis} = 25$ Hz, $^2J_{PP\text{-}cis} = 19$ Hz, $^1J_{PW} = 235$ Hz) and −26.3 ppm ($^2J_{PP\text{-}trans} = 159$ Hz, $^2J_{PP\text{-}cis} = 18$ Hz, $^1J_{PW} = 451$ Hz) indicating that all phosphorus nuclei coordinate to the tungsten centre and are chemically inequivalent and in meridional positions. The P atom corresponding to the signal at −11.5 ppm is located between the other two. Furthermore, in the ^1H NMR spectrum the NH proton was shifted to 10.87 ppm somewhat up-field in comparison to the free dmpi ligand and in the ^{13}C NMR spectrum two distinct resonances are assigned to the imidazole carbon atoms bearing the phosphorus substituents. They appear as a doublet of doublet of doublet at 157.0 ppm ($^1J_{CP} = 66$ Hz, $^2J_{CP} = 33$ Hz, $^3J_{CP} = 7$ Hz) for the bdmpi and as a doublet signal at 150.9 ppm ($^2J_{CP} = 48$ Hz) for the dmpi ligand. The spectroscopically derived structure of **1** was in full agreement with the structure obtained from the single crystal X-ray diffraction analysis.

A ligand substitution related to Scheme 2 was then attempted starting from $W(Cl)(NO)[P(OMe)_3]_4$ [19] and dmpi in THF at 70 °C. After 10 d the reaction was complete and the NMR spectra of the mixture showed that several compounds were formed. The crystallization of the crude product in a THF solution at −30 °C gave two main products subsequently in a turn of $[W(Cl)(NO)(dmpi)_4] \cdot 2THF$ ($\mathbf{2} \cdot 2THF$) as a crystalline form and $[W(Cl)(NO)(bdmpi)(dmpi)_2]$ (**3**) (Scheme 3) as powder. The latter was purified again by recrystallization from CH_3CN giving crystals of $\mathbf{3} \cdot CH_3CN$.



Scheme 1.



Scheme 2.