

Molybdenum and tungsten complexes of the neutral tripod ligands HC(pz)₃ and MeC(CH₂PPh₂)₃

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Abstract

Starting from [M(CO)₆], seven-coordinated complexes of tungsten and molybdenum containing the facially coordinating ligands HC(pz)₃ (**1**) and MeC(CH₂PPh₂)₃ (**2**) were obtained in a two-step reaction sequence. The complexes have a 4:3 piano stool geometry with almost perfect C₅ symmetry in the crystal. In solution, they show the typical fluxional behavior for seven-coordinated complexes even at low temperature. Complete oxidative decarbonylation occurs when [HC(pz)₃Mo(CO)₃] (**4**) or [MeC(CH₂PPh₂)₃Mo(CO)₃] (**6**) are treated with an excess of I₂ or Br₂.

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1. Introduction

Besides Cp, tris(pyrazolyle)borate (Tp) is the most widely used monoanionic facially coordinating tripod ligand in organometallic chemistry. Due to its shape, the Tp ligand and analogous systems are often called scorpionates. Since its first synthesis by Trofimenko in the late 1960s, a variety of different organometallic complexes containing Tp have been prepared [1–6]. Recently, homoscorpionate ligands with thioether [7,8], thiocarbonyl [9,10] or phosphine [11,12] donors have been reported, as well as NNS and NNO heteroscorpionates [13–15]. While the former were developed to obtain Tp analogues with a softer donor atom, the latter ones were introduced to act as molecular models for metalloproteins.

However, only few reports deal with the neutral analogue of Tp, tris(pyrazolyle)methane HC(pz)₃ (**1**), although its ability to act as a tridentate ligand in transition metal complexes has been observed virtually at the same time [16]. This is partially due to the difficulties associated with the syntheses of **1**, limiting the application compared to Tp

so far. Since a new, easy multi-gram scale preparation method has been reported, the interest on this neutral tripod ligand will increase [17,18].

Mo and W carbonyl complexes containing the Tp ligand have been extensively studied, and some similar HC(pz)₃ (**1**) complexes were prepared to compare the reactivities towards oxidative addition. This would open a new route to Mo(II) and W(II) as well as Mo(III) complexes. Furthermore, the tripod phosphine ligand 1,1,1-tris(diphenylphosphinomethyl)ethane MeC(CH₂PPh₂)₃ (**2**) was also employed in this study to compare the different donor atoms nitrogen and phosphorus.

2. Results

2.1. Precursors

The ligands **1** and **2** were prepared according to the published procedures [18,19]. The reaction of the hexacarbonyls [Mo(CO)₆] and [W(CO)₆] with **1** in refluxing DMF proceeds smoothly to give the neutral tricarbonyl complexes [HC(pz)₃M(CO)₃] (**3** and **4**) in high yields as yellow, air-stable solids [16]. The same reaction conditions can be

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used for the preparation of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3]$ (**5** and **6**), which are isolated as white, air-stable powders. This one step method is superior to previously reported synthetic procedures [20,21], giving higher yields in a shorter time period (Equation 1).

2.2. Crystal and molecular structure of **5**

Colorless, block-shaped crystals suitable for X-ray analysis of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{W}(\text{CO})_3]$ (**5**) were grown from dichloromethane/pentane at 20 °C. The complex crystallizes in the hexagonal space group R3 and has a crystallographic C_3 symmetry. Due to steric interaction, the octahedral geometry around the tungsten atom is distorted, with C1–W–C1A and P1–W–P1A angles significantly smaller than 90°. All these features, including the C_3 symmetry, have already been observed in the crystal structure of **6** [19] (see Fig. 1).

2.3. Oxidative addition

Reaction of $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3]$ (**3** and **4**) with I_2 or Br_2 gives the seven coordinated cationic complexes $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3\text{X}]\text{X}$ (M = W **7a, b**; Mo **8a, b**) as yellow or brown powders in good to excellent yields after 2 h at 20 °C (Equation 2, left). The iodo complexes **7a** and **8a** are stable as solids, while the bromo complexes are more sensitive towards air, decomposing within 3–5 days upon exposure.

When $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3]$ (**5** and **6**) is reacted with 1 equiv. of I_2 or Br_2 , IR spectroscopy reveals the formation of a 1:1 mixture of the starting material and the seven coordinated product. A second equivalent of halogen is necessary to complete the reaction within 2 h at 20 °C (Equation 2, right). The product complexes $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{M}(\text{CO})_3\text{X}]_3$ (M = W **9a, b**; Mo **10a**) are isolated in high yields as orange red or brown powders.

The $\text{HC}(\text{pz})_3$ complexes are more stable in solution than the $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$ complexes, allowing a complete characterization by IR and NMR spectroscopy even in acetone. The phosphine complexes **9a**, **9b** and **10a** can be isolated, but their characterization is difficult due to dehalogenation and subsequent decomposition. Only **9a** is stable enough to perform ^{13}C NMR spectroscopy, and even there, reformed starting material **5** is always observed within 6–8 h.

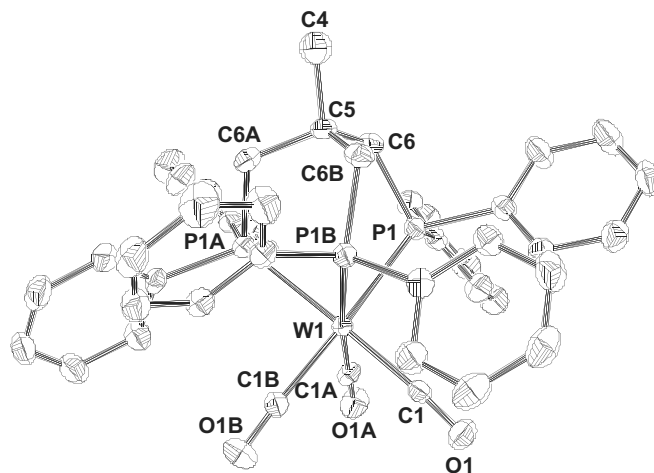


Fig. 1. Molecular structure of $[\text{MeC}(\text{CH}_2\text{PPh}_2)_3\text{W}(\text{CO})_3]$ (**5**), selected bond lengths (pm) and angles (°): W1–C1 197.8(4), W1–P1 250.69(11), C1–O1 114.1(4), P1–C6 185.2(3); C1–W1–P1 98.70(11), C1A–W1–P1 91.99(12), C1B–W1–P1 174.97(13), C1–W1–C1A 85.41(16), W1–C1–O1 175.4(4), P1–W1–P1A 84.12(4), W1–P1–C6 111.20(11).

2.4. Crystal and molecular structure of **7a**

See Fig. 2.

2.5. Crystal and molecular structure of **7b**

See Fig. 3.

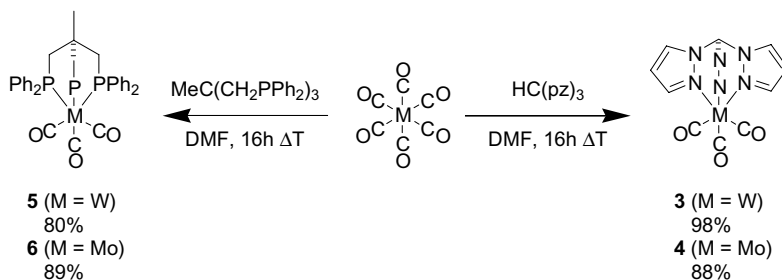
2.6. Crystal and molecular structure of **8a**

See Fig. 4.

2.7. Crystal and molecular structure of **9a**

See Fig. 5.

Crystals suitable for X-ray analysis have either been obtained from acetone/diethyl ether at 20 °C (**7a**) or –30 °C (**7b, 8a, 9a**). In **7b** and **9a**, acetone is found in the unit cell. The composition of the counter ions (X^- or X_3^-) is proven by the crystal structure. The two iodo complexes $[\text{HC}(\text{pz})_3\text{M}(\text{CO})_3\text{I}]\text{I}$ (M = W **7a**, Mo **8a**) are isostructural (monoclinic space group $P2(1)/c$, nearly identical cell parameters), while the bromo complex



Equation 1. Synthesis of the tricarbonyl complexes **3–6**.

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