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Studies on the formation of uniform η^3-coordinated triphos-Mo(0)-complexes [1]

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Abstract

A comparative study on the reaction of $(CO)_3Mo(CH_3CN)_3$ with a series of homologous chiral and prochiral trisphosphines is presented. Only one of the tripodal ligands formed the desired unique complex $(CO)_3Mo(\eta^3$-triphos) (**3b**) being the first example of a Mo(0)-complex containing a seven- as well as an eight-membered chelate ring. Spectroscopic properties of this complex and two different η^2-coordinated species are discussed. The molecular structure of the η^3-coordinated complex **3b** has been determined by X-ray crystallography. © 1998 Elsevier Science S.A.

Keywords: Tripodal ligands; Trisphosphines; Molybdenum(0); Nuclear magnetic resonance

1. Introduction

Metal complexes based on trisphosphines are intriguing compounds, extensively investigated in stoichiometric and catalytic reactions [1]. In addition, they also have relevance in neuronal networks as unique model receptors with definite conformational clefts [2]. Tridentate phosphines [3] offer distinct advantages over related bidentate ligands such as superior coordinating properties by the increased chelate effect and improved opportunities to control the stereochemistry and stoichiometry of the complexes formed. An important feature of tridentate phosphine ligands in reactions is their ability to create vacant coordination sites on the metal by the temporary cleavage of one phosphine–metal bond to afford η^2-coordinated complexes ('arm-off reaction') [4].

To avoid the formation of varying geometric, especially bridging species or diastereomeric complexes, hitherto, preferentially tripodal ligands forming smaller chelate rings (five- or six-membered rings) have been utilized [5–8]. Moreover due to this reason, the construction of mixed chelate rings has been rarely envisaged, although the latter offer interesting dynamic properties due to their different thermodynamic and kinetic stabilities [9]. A remarkable exception involving a mixed complex consisting of a five- and a six-membered chelate was obtained by Brunner when (*R*)-1,2,4-tris(diphenylphosphino)butane was reacted with $(CO)_3Cr(CH_3CN)_3$ [10]. The application of other chiral triphos ligands was reported by Huttner et al. [11–14]. However, in the ligands employed, the asymmetry was restricted to the phosphorus atom due to a neopentane framework, while the backbone remained C_3-symmetric. To our knowledge, systematic studies based on triphos-complexes have not been reported in the literature so far.

Recently, we described the synthesis of the chiral and prochiral trisphosphines (*R*,*R*)-**1a-e** and (*S*,*R*)-**2a**,**b** in order to complete our chemical library stocking differently shaped tridentate ligands [15–20]. Herein, we report on the reaction of these homologous phosphines with Mo(0) with the aim to show the topological re-

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[1] Dedicated to Prof. Dr. G. Huttner on the occasion of his 60th birthday.

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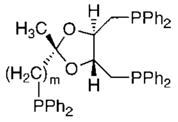
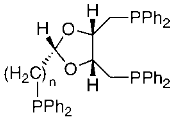
quirements necessary for the construction of a η^3-coordinated molybdenum complex [21,22].



(R,R)-1	a	b	c	d	e
m	2	3	4	5	6



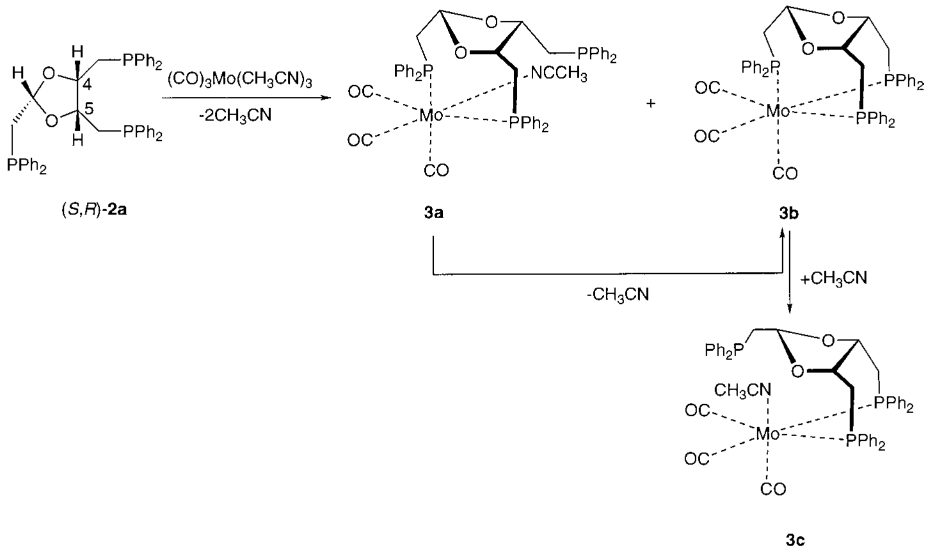
(S,R)-**2a** (n = 1)
(S,R)-**2b** (n = 2)

2. Results and discussion

The trisphosphines were heated with $(CO)_3Mo(CH_3CN)_3$ in CH_2Cl_2 for 3 h to afford colourless powders after evaporation of the volatiles. The former were investigated by ^{31}P-NMR-spectroscopy in [D_6]-benzene. It was disappointing to see that under the conditions applied the chiral phosphines (*R*,*R*)-**1a**–**e** and the prochiral analogue (*S*,*R*)-**2b** yielded mixtures of numerous molybdenum complexes. Because of the complexity owing to the signals at δ 32.0, 15.5, −15.0, and −23.1 single species could not be definitively assigned. This is a clear indication that different bridging and chelating modes of coordination occurred. Apparently, the structures of the trisphosphines, even those of the long-chain homologues **1d**,**e** did not match the coordinative demands for the desired molybdenum complex. All attempts to crystallize single complexes from different solvents failed.

In contrast, the reaction of $(CO)_3Mo(CH_3CN)_3$ with the trisphosphine (*S*,*R*)-**2a** featuring the highest degree of symmetry among the ligands investigated yielded distinguished species after heating in CH_2Cl_2 for 3 h. The ^{31}P-NMR spectrum of a sample recorded in $CDCl_3$ showed the presence of only two complexes **3a** and **3b** integrated as about 1:9. For **3b** a doublet at δ 21.2 ($^2J_{pp}$ = 28.2 Hz) and a triplet at δ 6.4 ($^2J_{PP}$ = 28.2 Hz) were observed. The down-field shift of the signals indicates that all phosphors atoms are bound to the metal. In this way besides a seven-membered ring an eight-membered chelate was formed. The other complex (**3a**) exhibited two doublets at δ 18.8 ($^2J_{PP}$ = 28.2 Hz) and 15.4 ($^2J_{PP}$ = 28.2 Hz), respectively. The singlet at δ −21.7 consistent with a noncoordinated phosphine group belonged to the latter complex too and gives proof that the tridentate ligand can act also in a bidentate manner. The resonances characterize **3a** as a Mo-complex wherein one of the stereochemically equivalent methylenphosphine groups of C(4) or C(5), respectively, and the third ligating group at C(2) formed an eight-membered chelate. Obviously, this complex is a key intermediate during the stepwise replacement of the three acetonitrile ligands by the trisphosphine. Since a prochiral triphos-ligand had been applied **3a** is asymmetric. The detection of **3a** gives evidence that the eight-membered ring is preferentially formed prior to the seven-membered chelate based on the vicinal methylenphosphine groups (kinetic product). Prolonged heating of **3a** in CH_2Cl_2 produced the η^3-coordinated complex **3b**.

Crystals from **3b** could be obtained by crystallization from benzene. The structure of the neutral complex was determined by single-crystal X-ray structural analysis. It possesses several interesting features as shown in Fig. 1 along with selected bond lengths and interbond angles. The three phosphorus atoms are bound to the metal in a facial mode. Together with three CO ligands a coordination number of six is achieved. The distances between the three phosphorus atoms and the molybdenum are in



Scheme 1.

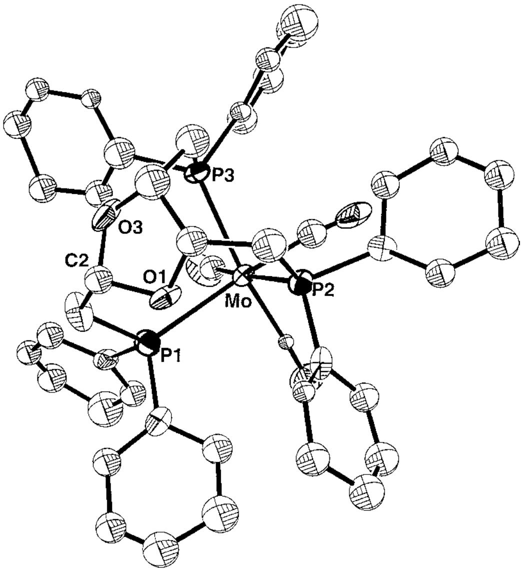


Fig. 1. Molecular structure of *fac*-$(CO)_3Mo(\eta^3$-((*R*,*S*)-2a) (**3b**). Hydrogen atoms have been omitted for clarity. Selected distances (Å): P(1)–Mo 2.6206(11), P(2)–Mo 2.5659(11), P(3)–Mo 2.5827(11), P(1)–P(2) 3.887(9), P(1)–P(3) 3.889(0), P(2)–P(3) 3.674(9). Selected angles (deg): P(3)–Mo–P(2) 91.51, P(2)–Mo–P(1) 96.29, P(3)–Mo–P(1) 97.18, O(3)–C(2)–O(1) 107.62.

the same range, whereby the distance of Mo(1)–P(1) [2.6206(11) Å] is slightly longer than those of Mo(1)–P(2) [2.5659(11) Å] or Mo(1)–P(3) [2.5827(11) Å], respectively. The widening of the geminal P–Mo–P angles (ranging from 91.5° to 97.2°) caused a distortion of the octahedral environment around the metal. The binding mode observed is rendered by the envelope conformation of the 1,3-dioxolane backbone. A most remarkable feature of the complex is that the O(1)–C(2)–O(3) core is folded opposite to the metal. This can be deduced from the angles C(4)–O(1)–C(2) [109.0(3)°] and C(5)–O(3)–C(2) [106.7(3)°]. In this conformation the methylenphosphine unit bound to C(2) occupies a nearly ideal equatorial position. In contrast to this arrangement the vicinal methylene groups are placed pseudo-axially on the 1,3-dioxolane ring. Of particular interest is that brief heating of the η^3-coordinated complex in an excess of acetonitrile caused the substitution of only one phosphorus by acetonitrile and the predominant formation of the $(CO)_3Mo(CH_3CN)(\eta^2$-triphos) complex **3c**. In the ^{31}P-NMR spectrum of a sample taken from the reaction mixture singlets at δ 25.8 and -25.1, respectively, were observed. This result indicates that **3c** has a plane of symmetry. In contrast to the chiral η^2-coordinated species described above (eight-membered ring), here the vicinal alkylphosphine groups form the ring with the molybdenum (seven-membered chelate). Obviously, the latter represents the thermodynamic product.

In summary, our results clearly demonstrate the high importance of the appropriate geometry of the tripodal ligand in order to create a uniform η^3-coordinated Mo-complex. Moreover, it is shown that even non-symmetric tripodal ligands designed for the formation of large ring-sizes are capable to form uniform η^2-coordinated species. The geometry of the latter depends upon the reaction conditions applied. We are currently exploring the complexation behaviour of other metals and the employment of the effects described in catalytic reactions.

3. Experimental section

All reactions and manipulations have been carried out in an atmosphere of pure and dry argon using standard Schlenk procedures. CH_2Cl_2 was predried and freshly distilled before use. The ligands were synthesized by literature procedures [20]. $(CO)_3Mo(CH_3CN)_3$ was prepared according to Ref. [21] by the reaction of $Mo(CO)_6$ with an excess of acetonitrile. It is important to note that only a sufficiently long reaction time and careful isolation of the Mo-complex at low temperature gave a satisfying quality of the desired complex without the formation of appreciable amounts of side products such as $(CO)_4Mo(CH_3CN)_2$. NMR spectra were recorded on a Bruker ARX 400 spectrometer. The IR spectrum was measured on a IR 550 Nicolet spectrometer.

3.1. *fac-Tricarbonyl-η^3-[cis,cis-2,4,5-tris(diphenylphosphinomethyl-1,3-dioxolane]molybdenum (**fac**-$(CO)_3Mo(\eta^3$-((S,R)-2a) (**3b**)*

Trisphosphine (*S*,*R*)-**2a** (0.200 g, 0.299 mmol) in CH_2Cl_2 (15 mL) reacted with $(CO)_3Mo(CH_3CN)_3$ (0.091 g, 0.299 mmol) for 6 h under reflux at an oil bath temperature of 100°C. Then the volatiles were distilled off. The residue was dried under vacuo and recrystallized from benzene to give colourless crystals (0.27 g, 90% yield). mp > 250°C; $C_{45}H_{39}MoO_5P_3 \cdot 2C_6H_6$ (1004.83): calc. C 68.13, H 5.12, found C 67.85, H 4.78.

3.1.1. *Spectroscopic data*

^{1}H NMR (400.13 MHz, [D$_6$]benzene) δ: 7.40–7.10 (m, 30H, Ar), 5.28 (m, 1H, CH), 4.60 (m, 2H, CH), 3.24 (m, 2H, CH_2), 2.50 (2H, dd, $J = 8.7$, 2.6 Hz, CH_2), 2.25 (2H, d, $J = 5.6$ Hz, CH_2); ^{13}C{^{1}H} NMR (100.63 MHz, [D$_6$]benzene) δ: 132.9–127.9 (Ar), 101.0 (CH), 76.1 (CH), 32.9 ($^1J_{PC} = 10.6$ Hz, CH_2), 29.9 (d, $^1J_{PC} = 11.1$ Hz, CH_2); ^{31}P{^{1}H} NMR (161.99 MHz, [D$_6$]benzene) δ: 21.2 (d, $^2J_{PP} = 28.2$ Hz), 6.4 (t, $^2J_{PP} = 28.2$ Hz); IR (nujol) 1931, 1898, 1823 cm^{-1} (C=O).

3.1.2. *Crystal structure determination of **3b***

X-ray data of **3b**: Siemens P4-Diffractometer, graphite monochromated Mo-$K\alpha$-radiation. Substance crystallizes with two solvent benzenes per complex molecule, one solvent being in disordered position. Data collection in routine scan ω-scan at 233 K. Structure solution in $P\bar{1}$ with direct methods of SHELXTL [23], refinement against F^2, SHELXL-93 [24], refinement calculation in $P\bar{1}$ after shifting the origin, structure representation: SHELXTL (Siemens), $0.6 \times 0.44 \times 0.22$ mm, colourless prism, space group $P\bar{1}$, #2, triclinic, $a = 9.954(1)$, $b = 15.352(2)$, $c = 16.938(1)$ Å, $V = 2433.3(4)$ Å^3, $Z = 2$, $\rho_{\text{cal.}} = 1.371$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 0.418$ mm^{-1}, 11832 collected, 5961 unique reflections, observed 4950 $[I > 2\sigma(\mathrm{I})]$, $R_1 = 0.0433$ (observed) $R_1 = 0.0556$ (all), wR^2 (all data) $= 0.1155$, 651 parameters, 18 restraints.

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