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Preliminary communication

Synthesis and X-ray molecular structure of *cis,cis*-1,3,5-Tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane

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Abstract

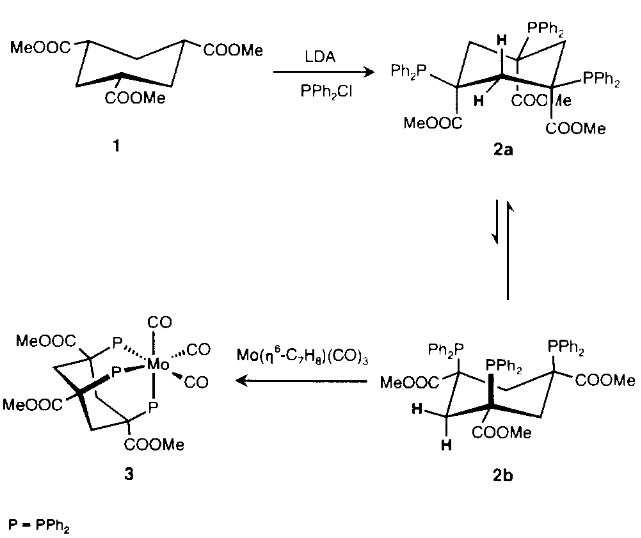
The novel tripodal phosphine ligand *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (tdppcyme) (2) has been synthesized. ^{1}H, ^{13}C and ^{31}P NMR spectroscopy shows that in solution the sterically demanding diphenylphosphine groups occupy equatorial positions on the cyclohexane ring. An X-ray crystal investigation confirms this result for the solid state. Treatment of tdppcyme with $Mo(\eta^6\text{-}C_7H_8)(CO)_3$ gives $Mo(tdppcyme)(CO)_3$ (3), with octahedral molybdenum coordination.

Keywords: Molybdenum; Tripodal phosphine; Crystal structure

1. Introduction

The preparation of the new tripodal phosphine ligand *cis,cis*-1,3,5-tris(diphenylphosphino)cyclohexane (tdppcy) has opened up the synthetic pathway to octahedral and trigonal bipyramidal metal complexes with adamantane-type structures [1]. However, the poor yield of tdppcy has hampered the investigation of these adamantane-type complexes. A circumvention of this drawback is possible by the functionalization of the cyclohexane ring at the 1,3,5 positions with electron-withdrawing groups. The stabilization of adjacent carbanions allows facile *ipso* functionalization and opens up a new route to tripodal phosphine ligands with cyclohexane as backbone (Scheme 1). In addition, functional groups at the *ipso* positions of the cyclohexane ring offer the opportunity to study their influence on the complexation behavior of the phosphines and the reactivity of the resulting complexes. They can be further modified to control the solubility and may be used as spacers to support the metal complexes.

According to Scheme 1, *cis,cis*-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (tdppcyme) (2) can be synthesized by α deprotonation of the triester 1 with lithium-diisopropylamide and subsequent treatment with chlorodiphenylphosphine. To retain the configuration at the α-C atoms it is important to control the temperature (−10°C) rigorously during the reaction. The colorless phosphine 2 is thermally stable and dissolves in toluene, methylene chloride, acetone, tetrahydrofuran and acetonitrile.



Scheme 1.

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[1] X-ray structure analysis.

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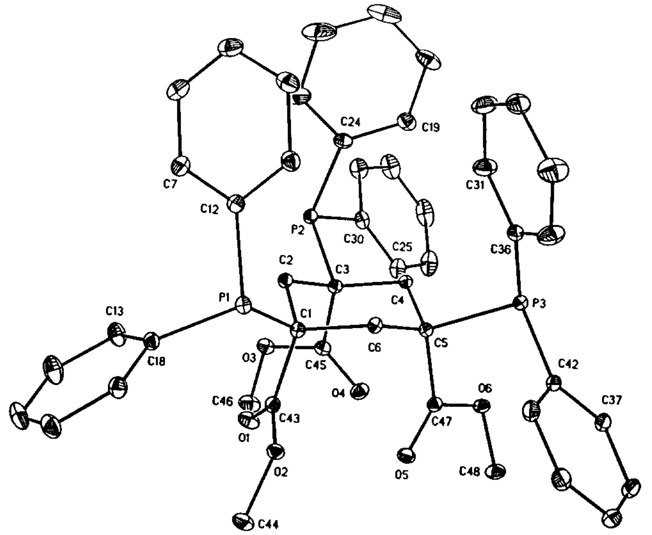

Fig. 1. ORTEP plot of **2**. Selected bond distances, bond angles and torsional angles are as follows: P(1)–C(1), 193.9(2) pm; P(2)–C(3), 192.0(2) pm; P(3)–C5, 194.6(2) pm; C(1)–C(2)–C(3), 116.09(12)°; C(3)–C(4)–C(5), 115.93(11)°; C(5)–C(6)–C(1), 115.77(12)°; C(3)–C(2)–C(1)–C(6), 50.0(1)°; C(1)–C(2)–C(3)–C(4), 50.5(1)°; C(5)–C(4)–C(3)–C(2), 49.2(2)°; C(3)–C(4)–C(5)–C(6), −48.5(1)°; C(1)–C(6)–C(5)–C(4), 47.5(2)°, C(2)–C(1)–C(6)–C(5), −48.2(1)°.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of tdppcyme are in agreement with the *cis,cis* arrangement of the functional groups on the cyclohexane ring. The alkane region of the ^{13}C{^{1}H} NMR spectrum displays a triplet ($\delta = 37.8$ (^2J(PC) = 18.8 Hz) ppm) and a doublet of triplets ($\delta = 47.0$ (^1J(PC) = 26.9 Hz, ^3J(PC) = 9.5 Hz) ppm) which are caused by the interaction of the three methylene and the three quarternary carbon atoms with the phosphorus nuclei respectively. In addition the ester carbonyl atoms are observed as a doublet ($\delta = 173.6$ (^2J(PC) = 3.3 Hz) ppm) and the methyl groups as a singlet ($\delta = 51.6$ ppm). The most characteristic feature in the ^{1}H NMR spectrum of **2** is the large difference of the chemical shift ($\Delta\delta = 1.67$ ppm) of the two ring methylene protons. Such a difference of the chemical shift is consistent with the different orientation of the two protons with respect to the acyl groups (Scheme 1, **2a**) [2]. This indicates that in solution the ester functional groups prefer the axial positions, and the diphenylphosphine groups the equatorial orientation [2]. This is also confirmed by the small vicinal P–H coupling constants (^3J(PH) = 8.8, < 4 Hz) observed for the ring methylene protons [3]. In the IR spectrum (KBr) of **2**, one strong absorption is observed for $\nu(COOCH_3)$ at 1725 cm^{-1}.

An X-ray structure analysis performed on crystals of **2** establishes the connectivity of the atoms (Fig. 1) [4]. As demonstrated by NMR spectroscopy in solution, the ester functional groups are oriented triaxially, and the diphenylphosphine groups occupy the equatorial sites of the cyclohexane ring in the crystal. The endocyclic bond angles at the ring CH_2 carbon atoms are widened to 115.93° (average) compared with 111.5° in cyclohexane [5]. This leads to a change in the torsional angle to ±48.5° (average value) which indicates that the chair conformation of the cyclohexane ring in **2** is flattened compared with cyclohexane (torsional angel ±55°) [5].

Treatment of tdppcyme with $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ in hot toluene gives **3** with octahedral coordination at molybdenum (Scheme 1) as a colorless powder. The tricarbonyl complex **3** is only soluble in pyridine. The facial coordination of tdppcyme is demonstrated by the two ν(CO) absorptions which are observed in the IR spectrum of **3** at 1939 and 1856 cm^{-1} respectively [6]. The C_{3v} symmetry of the molybdenum complex **3** is also confirmed in the ^{1}H, ^{31}P and ^{13}C NMR spectra. The ^{31}P{^{1}H} NMR spectrum displays a singlet with a typical coordination chemical shift [1]. Because of the poor solubilty of **3**, a solid state ^{13}C CP MAS NMR spectrum has been recorded which shows singlets for the quarternary ring carbon atoms, the methyl and the ring methylene groups, the ester carbonyl atoms and the CO groups at the metal center.

2. Experimental details

2.1. General procedures

All manipulations were performed under pure argon using Schlenk techniques. Toluene and diethylether were freshly distilled from sodium–benzophenone, diisopropylamine from CaH_2, and *n*-pentane from $LiAlH_4$ prior to use. Literature methods were used for the preparation of *cis,cis*-1,3,5-trimethyl-cyclohexane-1,3,5-tricarboxylate [7] and $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ [8].

Mass spectra were measured as follows: FD, Finnigan MAT 711A modified by AMD; fast atom bombardment (FAB), Finnigan TSQ 70. The IR spectra were obtained with a Bruker IFS 48. ^{31}P{^{1}H} NMR measurements were made with a Bruker WP 80 and an AC 80 (32.39 and 32.44 MHz; external standard, 1% H_3PO_4–acetone-d_6). ^{1}H and ^{13}C{^{1}H} NMR data were collected with a Bruker AC 250 (250.13 and 62.90 MHz; chemical shifts were measured relative to partially deuterated solvent peaks which were referenced to tetramethylsilane). ^{31}P and ^{13}C CP MAS results were obtained with a Bruker ASX 300. The single-crystal X-ray structure determination was carried out with a Siemens P4 diffractometer, and the elemental analysis with a Carlo Erba 1106.

2.2. *cis,cis-1,3,5-Tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane (2)*

A solution of 0.85 ml (6.0 mmol) of diisopropylamine in 25 ml of diethylether which was cooled to

−10°C was treated with 3.75 ml of a 1.6 M solution of ^{n}BuLi-n-hexane within 15 min. The off-white mixture was stirred for another 15 min and a −10°C solution of **1** (0.52 g, 2.0 mmol) dissolved in 100 ml of diethylether was added dropwise over a period of 2 h. After the off-white suspension had been stirred for an additional 30 min, a solution of chlorodiphenylphosphine (1.1 ml, 6.0 mmol) in 50 ml of diethylether kept at −10°C was added dropwise. The suspension was allowed to warm to room temperature for 12 h. The reaction mixture was reduced in volume to 100 ml, washed twice with 50 ml of degassed water, once with 50 ml of HCl (50 ml H_2O : 1 ml HCl 32%), and three times with 50 ml of degassed water. The precipitate was filtered, washed three times with 15 ml of cold diethylether and dried in vacuo, (yield, 1.215 g (74.9%); melting point (m.p.), 174°C (decomposition)). $^{31}P\{^1H\}$ NMR (toluene, −30°C): δ 26.5 (s) ppm. ^1H NMR (CD_2Cl_2): δ 1.5 (dt, $^2J(HH) = 14.0$ Hz, $^3J(PH) = 8.8$ Hz, 3 H, CHH_a), 3.1 (br d, $^2J(HH) = 14.0$ Hz, $^3J(PH) < 4$ Hz, 3 H, CHH_e), 3.2 (s, 9 H, $COOCH_3$), 7.2–7.5 (m, 30 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2); δ 37.8 (t, $^2J(PC) = 18.8$ Hz, CH_2), 47.0 (dt, $^1J(PC) = 26.9$, $^3J(PC) = 9.5$ Hz, CP), 51.6 (s, CH_3), 128.8 (d, $^3J(PC) = 7.5$ Hz, m-C_6H_5), 129.6 (s, p-C_6H_5), 134.9 (d, $^1J(PC) = 22.3$ Hz, *ipso*-C_6H_5), 135.1 (d, $^2J(PC) = 22.2$ Hz, o-C_6H_5), 173.6 (d, $^2J(PC) = 3.3$ Hz, $COOCH_3$) ppm. IR (KBr): $\nu(COOCH_3)$ 1725 sst cm^{-1}. Anal. Found (molecular mass (FAB), 811.1): C, 70.76; H, 6.09. $C_{48}H_{45}O_6P_3$ Calc.: (molecular mass, 810.80): C, 71.11; H, 5.59%.

2.3. Tricarbonyl[cis,cis-1,3,5-tris(diphenylphosphino)-1,3,5-tris(methoxycarbonyl)cyclohexane]molybdenum (3)

A mixture of equimolar amounts of $Mo(CO)_3(\eta^6$-$C_7H_8)$ (54.4 mg, 0.2 mmol) and tdppcyme (162.2 mg, 0.2 mmol) in 20 ml of toluene was kept at 75°C for 2 h, during which a colorless precipitate was formed. This was collected on a sintered glass frit, washed twice with 15 ml of toluene, three times with 10 ml of n-pentane and dried in vacuo, (yield, 184.9 mg (93.3%); m.p., 256°C (decomposition). ^1H NMR (pyridine): δ 2.5–2.8 (br m, 3 H, CHH_a), 3.2 (s, 9 H, CH_3), 3.2–3.4 (br m, 3 H CH_eH), 7.0–7.7 (m, 30 H, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (pyridine, −30°C): δ 39.9 (s) ppm. ^{31}P CP MAS NMR: δ 40.7 (s) ppm. ^{13}C CP MAS NMR: δ 32.9 (s, CH_2), 47.7 (s, CP), 50.3 (s, CH_3), 129.3–139.4 (m, C_6H_5), 172.7 (s, $COOCH_3$), 219.3 (s, CO) ppm. IR (KBr): $\nu(CO)$ 1939 sst, 1856 sst, $\nu(COOCH_3)$ 1716 st cm^{-1}, Anal. Found: (molecular mass (FAB), 992.3; $[M^+]$ (^{98}Mo)): C, 61.13; H, 4.37. ($C_{51}H_{45}MoO_9P_3$ Calc. (molecular mass, 990.77): C, 61.83; H, 4.58%.

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[4] Crystal data for **2**: $C_{48}H_{45}O_6P_3$; $M = 810.75$; monoclinic; space group, $P2_1/c$; $a = 1119.1(4)$, $b = 1338.2(5)$, $c = 2763.9(9)$ pm, $\beta = 93.42(3)°$; $V = 4.132(3)$ nm^3; $Z = 4$, $D_c = 1.303$ Mg m^{-3}; $F(000) = 1700$; Mo Kα radiation, $\lambda = 0.71073$ mm^{-1}, $\mu = 0.194$ mm^{-1}. The data were collected on a Siemens P4 diffractometer. 14545 reflections were measured, with 2θ in the range 4–50°, 5809 having $I > 2\sigma(I)$, were used in the refinement. The structure was solved by direct methods. The hydrogen atoms were placed at the calculated positions. The R and wR_2 values were 0.0317 and 0.0801 respectively. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-58441, the names of the authors and the journal citation.

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