Optically Active Transition Metal Compounds, 136 [1]. An Octahedral Molybdenum Complex (P-P')$Mo(CO)_4$ with a Chiral Secondary Phosphorus Atom

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Reaction of (η^6-$C_6H_5CH_3$)$Mo(CO)_3$ with the easily accessible chiral chelate ligand *P,P,P'*-tris-[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene P-P' afforded the octahedral molybdenum carbonyl derivate (P-P')$Mo(CO)_4$ **1** as a diastereomer mixture **1a** (74%) and **1b** (26%). Crystallization gave single crystals of (S_P)-(P-P')$Mo(CO)_4$ **1a**. The X-ray structure analysis of compound **1a** revealed the formation of an unusual triple-decker π-stack in the solid state.

Key words: Molybdenum, Chirality, Secondary Phosphorus, π-Stack, Triple-Decker

Introduction

In the presence of cobalt-phosphane catalysts 2,5-norbornadiene undergoes [2+2+2] homo-Diels-Alder reactions with acetylenes to give deltacyclenes. Using the procatalyst $Co(acac)_3$, the optically active cocatalyst (+)-Norphos and the reducing agent Et_2AlCl in THF the reaction of norbornadiene and phenylacetylene affords reliably (+)-8-phenyldeltacyclene with an enantiomeric excess of $> 97.5\%$ in gram quantities [2 – 4]. Subsequently, other catalytic systems and acetylenic substrates were used in this [2+2+2] homo-Diels-Alder reaction [5 – 12].

The double bond of (+)-8-phenyldeltacyclene permits further derivatization reactions, *e.g.* the addition of P-H bonds [10]. The reaction of 1,2-bis-(phosphanyl)benzene with a fourfold excess of (+)-8-phenyldeltacyclene does not give the fully substituted product with four deltacyclanyl substituents at the two phosphorus atoms. Due to steric hindrance the reaction stops after three P-H additions [10]. The resulting trisubstitution product *P,P,P'*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene P-P' is an unsymmetrical chelate ligand consisting of a tertiary phosphorus atom and a chiral secondary phosphorus atom. In the P-H addition 8-phenyldeltacyclene becomes the (+)-9-phenyldeltacyclan-8-yl substituent according to a change of priorities of carbon atoms 8 and 9 of the deltacyclane skeleton. The (+)-sign implies that the P-substituted C atom of the (+)-9-phenyldeltacyclanyl groups has (*S*)-configuration, the phenyl-substituted C atom (*R*)-configuration etc. [13].

The trisubstituted ligand P-P' consists of $8 \times 3 = 24$ fixed chiral carbon centers in the three deltacyclanyl substituents and one labile stereogenic secondary phosphorus atom. Due to the well known configurational lability of secondary phosphanes fast epimerization takes place in the free ligand [14 – 16]. The diastereomer ratio of P-P' at room temperature in $CDCl_3$ is 64:36 (28% de) [13].

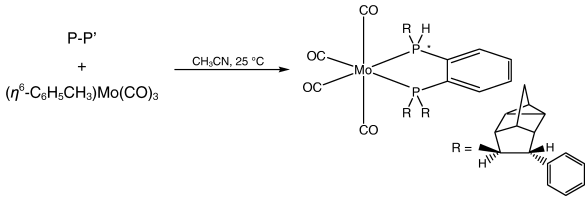
Mononuclear, dinuclear and unusual trinuclear nickel, palladium and platinum complexes of the ligand P-P' and its anion were reported in which the square planar M(II) arrangements did not contribute to stereogenicity [13, 17]. Recently, chiral-at-metal half-sandwich compounds of rhodium and iridium with P-P' have been synthesized and characterized [1]. In the present study the formation of two diastereomers of the octahedral $Mo(CO)_4$ complex of P-P' and the X-ray crystal structure of one of the diastereomers is reported [18].

Results and Discussion

Reaction of (η^6-$C_6H_5CH_3$)$Mo(CO)_3$ with the chelate ligand P-P' (molar ratio 1:1) afforded the octahedral molybdenum carbonyl derivate (P-P')$Mo(CO)_4$ **1** as a colourless powder in 18% yield (Scheme 1).

* X-ray structure analysis

Obviously, formation of (P-P')Mo(CO)$_4$ **1** from (toluene)Mo(CO)$_3$ involved an intermolecular carbonyl transfer.



Scheme 1. Synthesis of (P-P')Mo(CO)$_4$ **1**.

Compound **1** should consist of two diastereomers **1a** and **1b** differing in the configuration of the secondary phosphorus atom PRH of the chelate ligand P-P'. This was corroborated by the $^{31}P\{^1H\}$ NMR spectrum which gave rise to two AB patterns for each diastereomer at 27.1 and 68.4 ppm for **1a** (74%) as well as 32.4 and 69.4 ppm for **1b** (26%) with coupling constants $^2J_{PP} = 8.4$ for **1a** and 7.2 Hz for **1b**. The signals at higher ppm values are due to the phosphorus atoms of the PR_2 groups. The signals at lower ppm values were assigned to the stereogenic phosphorus atoms PRH on the basis of PH coupling ($^1J_{PH} = 320$ for **1a** and 321 Hz for **1b**).

Attempts to separate the diastereomers **1a** and **1b** by chromatography failed. However, crystallization was successful. Single crystals were obtained from a benzene solution of compound **1** suitable for X-ray analysis. In the $^{31}P\{^1H\}$ NMR spectrum a solution of the crystals showed only the AB pattern of the main diastereomer **1a**. There were no changes after one week. Thus, no epimerization leading to diastereomer **1b** did take place. Compound **1a** is configurationally stable at the secondary phosphorus atom.

The structure of the isolated diastereomer is shown in Figure 1. The coordination around the molybdenum center is octahedral with four carbonyl ligands and the bidentate ligand P-P' which occupies *cis*-positions. The dihedral angle P1-P2-C6-C7 $-9.11(10)^\circ$ indicates a slight distortion of the coordination sphere around the metal center such as to relieve steric strain. Applying the Cahn-Ingold-Prelog system the priority sequence for the stereogenic phosphorus atom is Mo > $C_{benzene}$ > C_Δ > H [19, 20] (the subscript Δ abbreviates the (+)-9-phenyldeltacyclanyl substituent). Thus, compound **1a** has (S_P)-configuration.

The Mo-C distances in (S_P)-**1** are 1.999(3), 1.991(3), 2.035(3) and 2.031(3) Å for C6, C7, C8 and C9 with C-O bond lengths in the range 1.146(4)–1.153(5) Å. The two Mo-P bonds are slightly different from each other, 2.475(1) for the PRH phosphorus atom P1 and 2.526(1) Å for the PR_2 phosphorus atom P2. The angles around the molybdenum center in the square P1-P2-C6-C7 are 80.27(3) P1-Mo-P2, 96.27(10) P2-Mo-C6, 91.30(14) C6-Mo-C7 and 92.82(10)° C7-Mo-P1. Obviously, the smallest angle is found for P1-Mo-P2 with a value comparable to those measured in chiral-at-metal half-sandwich Rh and Ir compounds of P-P' [1, 13, 18]. This is due to the geometry of the ligand, enforced by the 1,2-position of the coordinating phosphorus atoms P1 and P2 at the bridging benzene ring.

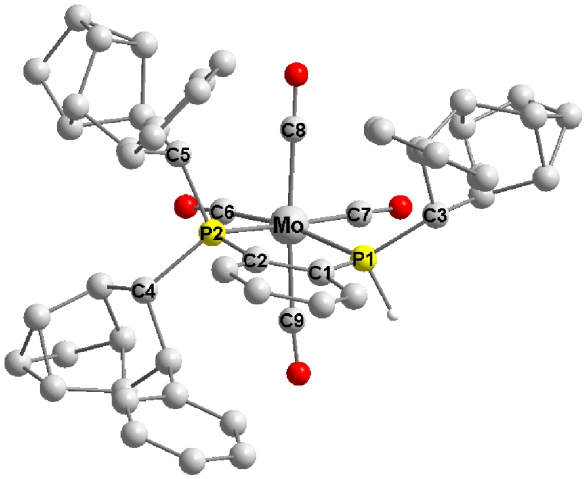


Fig. 1. Molecular structure of (S_P)-(P-P')Mo(CO)$_4$ **1a** without hydrogen atoms except P-H.

The M(P-P') chelate ring in compound **1**a is not planar but slightly puckered. This puckering results in helicity measured as the torsion angle P1-C1-C2-P2. For (S_P)-**1** this torsion angle is $-2.08(20)^\circ$ defining δ conformation. The C1 atom (PRH side) and the adjacent parts of the benzene ring tend to orient towards the less sterically hindred P-H side of the chelate ligand. Therefore, the helicity of the chelate ring is determined by the configuration of the stereogenic phosphorus atom P1. (S_P)-configuration enforces δ conformation and in contrast (R_P)-configuration should enforce λ conformation in the chelate ring [1].

Ligand P-P' is bulky and relatively rigid. Conformation-determining is rotation about the P-C_Δ bonds (and to a lesser extent rotation about the C_{ipso}-C_Δ bond). A measure of the rotation of the deltacyclanyl substituents about the P-C_Δ bond in compound

1a is the torsion angle Mo-P-C_Δ-C(Ph): Mo-P2-C5-C(Ph) = −179.68(19), Mo-P2-C4-C(Ph) = 63.64(22) and Mo-P1-C3-C(Ph) = 67.92(25)°. Interestingly, the phenyl rings of the deltacyclanyl groups C4 and C3 adopt positions such as to form a double π-stack with the phenylene system of the chelate ring in between. The three phenyl rings in the triple-decker are nearly parallel to each other with distances of 3.770 and 4.229 Å between the ring centers of the phenylene systems of the chelate ring and the participating phenyls.

Experimental Section

^{1}H NMR spectra: Bruker ARX-400 (400 MHz). ^{31}P NMR spectra: Bruker ARX-400 (162 MHz). Mass spectra: Finnigan MAT 95. Optical rotations: Perkin-Elmer 241 polarimeter. Elemental analyses: Elementar Vario EL III. X-ray structure analysis: STOE-IPDS diffractometer (Mo-K_α radiation, 173 K (Oxford cryosystems cooler [21], graphite monochromator), SIR-97 [22] and SHELXS-97.

*Synthesis of (P-P')Mo(CO)$_4$ (**1**)*

The chelate ligand P-P'=*P,P,P'*-tris[(+)-9-phenyldeltacyclan-8-yl]-1,2-bis(phosphanyl)benzene (359 mg, 0.50 mmol) and the molybdenum complex (η^6-$C_6H_5CH_3$)Mo(CO)$_3$ (138 mg, 0.41 mmol) were suspended in abs. acetonitrile CH_3CN (20 ml) in an atmosphere of dry nitrogen at room temperature and stirred for 10 h. The resulting solution was evaporated. The slightly brown residue was taken up in benzene for chromatography and eluted with petroleum ether/benzene (1:1) on a column loaded with SiO_2 (10 cm). Removing the solvent gave the colorless complex (P-P')Mo(CO)$_4$ (**1**) as a diastereomer mixture of **1a** (74%) and **1b** (26%). Yield 70 mg (18%). – M.p. > 235° dec. – IR (KBr) ν = 2040, 1995, 1985, 1965 (C≡O) cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6) diastereomer mixture **1a**/**1b**: δ = 0.29 – 4.16 (m, aliphat. H **1a**/**1b**), 5.34 (dt, $^1J_{PH}$ = 321 Hz, J = 9.1 Hz, PH **1b**), 5.63 (dt, $^1J_{PH}$ = 320 Hz, J = 5.5 Hz, PH **1a**), 6.06 – 7.41 (m, aromat. H **1a**/**1b**). – ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) diastereomer mixture **1a**/**1b**: δ = 27.1 (d, $^2J_{PP}$ = 8.4 Hz ($^1J_{PH}$ = 320 Hz), PRH **1a**), 32.4 (d, $^2J_{PP}$ = 7.2 Hz ($^1J_{PH}$ = 321 Hz), PRH **1b**), 68.4 (d, $^2J_{PP}$ = 8.4 Hz, PR_2 **1a**), 69.4 (d, $^2J_{PP}$ = 7.2 Hz, PR_2 **1b**). – MS (FD, CH_2Cl_2): *m/z* (%) = 934.7 (100) [M$^+$], 906.7 (25) [M$^+$-CO]. – $C_{55}H_{50}MoO_4P_2$ (932.8): calcd. C 70.89, H 5.40; found C 70.14, H 5.33.

Crystallisation from benzene afforded (S_P)-(P-P')Mo(CO)$_4$ **1a**. Optical rotation (c = 0.300, CH_2Cl_2) $[\alpha]_D^{RT}$ = +175, $[\alpha]_{578}^{RT}$ = +217, $[\alpha]_{546}^{RT}$ = +242, $[\alpha]_{436}^{RT}$ = +375.

*Molecular structure of (S_P)-(P-P')Mo(CO)$_4$ (**1a**)*

$C_{55}H_{50}MoO_4P_2$, translucent prisms with dimensions 0.36 × 0.28 × 0.24 mm, crystallizes in the orthorhombic space group $P2_12_12_1$ with the lattice parameters a = 11.1641(4), b = 11.5681(5), c = 34.2577(16) Å, V = 4424.3(3) Å^3, Z = 4, d = 1.401 g/cm^3, μ = 0.417 mm^{-1}. 57790 reflections collected in the range 2.12° ≤ 2θ = 25.89°; 8573 reflections independent, 7165 of which observed with $I > 2\sigma I$). Full matrix least squares refinement on F^2 with 563 parameters converged at $R1/wR2$-values of 0.032/0.072 (goodness of fit on F^2 = 0.945), absolute structure parameter: −0.04(3), no absorption correction. The max./min. residual electron density was 0.676/−0.293 e·Å^{-3}. CCDC 234283 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44/1223/336033.

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