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Synthesis and X-ray structure of (−)-[Mo(η^5-C_5Me_4-3-pinanyl)(CO)$_3$Me]

Richard Lai, Laurent Bousquet and Andreas Heumann

Université d'Aix-Marseille, Faculté de St.-Jérôme, URA 1410, ENSSPICAM, F-13013 Marseille (France)

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Abstract

Reaction of the methyl ester of (−)-pinane-3-carboxylic acid **1** with the lithium derivative of 2-bromobut-2-ene affords, after dehydration, an isomeric mixture of 3-pinanyl cyclopentadienes **3**. Successive treatment with Li^{n}Bu, Mo(CO)$_6$ and MeI gives rise to the title complex **5**, whose NMR spectra and X-ray structure unambiguously demonstrate the optical integrity and purity of this compound.

1. Introduction

Organometallic complexes bearing chiral ligands are of considerable interest in view of their potential application to asymmetric organic synthesis [1]. The η^5-cyclopentadienyl unit should be considered as one of the best ligands of potential use due to its strong covalent bonding to the metal [2]. Among the few methods leading to optically active cyclopentadienes [3], the chiral version [4] of Bercaw's Organic Synthesis protocol for 1,2,3,4,5,-pentamethylcyclopentadiene [5] is extremely promising. In this two-step synthesis, one of the five carbon-methyl units comes from the carboxylate function of an organic ester. We are developing a general approach to chiral polyalkylcyclopentadienes, using the chemical and physical advantages of persubstituted cyclopentadienes compared to the unsubstituted diene [6]. We chose the bridged bicyclic framework of pinane, well known for its use as a chiral auxiliary, and without problems of racemisation and isomerisation under basic and acidic reaction conditions. Treatment of the methyl ester of (−)-pinan-3-carboxylic acid **1** [7] with the lithium derivative of 2-bromobut-2-ene (*cis/trans* mixture) afforded the tertiary dienyl alcohols (+)-**2** (yield > 90%), a mixture of isomers, which was cyclized in the presence of $CuSO_4$-SiO_2 [8] at 20°C. The major compound of the (unseparable) product mixture was indeed the cyclopentadiene system **3**. Treatment of a THF solution of the crude olefinic mixture with Li^{n}Bu (1.6 M in hexane) led to the lithium cyclopentadienyl **4** as the sole lithiated product (white, extremely air-sensitive solid, *ca.* 70% yield).

Subsequent reaction [9] of **4** with molybdenum hexacarbonyl and methyl iodide afforded (−)-[Mo(η^5-C_5Me_4-3-pinanyl)(CO)$_3$Me] **5** (70% yield based on Mo(CO)$_6$), purified by column chromatography on silica). The formation of this transition complex is a supplementary proof of the structure of the cyclic dienes **3**. The ^{1}H and, in particular, the ^{1}H composite-pulse-decoupled ^{13}C NMR spectra of **5** are diagnostic for the optical purity of the molybdenum complex. These spectra indicate clearly that no epimerization had occured during the synthesis of the chiral cyclopentadienyl ligand. In the spectra, the signals as-

TABLE 1. Selected bond lengths (Å) for **5**

Mo–C(1) 1.95(2)	C(3)–O(2) 1.18(4)	C(14)–C(15) 1.60(2)
Mo–C(2) 1.94(2)	C(7)–C(8) 1.43(2)	C(14)–C(19) 1.60(2)
Mo–C(3) 2.03(3)	C(5)–C(6) 1.39(2)	C(15)–C(16) 1.55(2)
Mo–C(4) 2.40(2)	C(5)–C(9) 1.39(2)	C(15)–C(20) 1.54(2)
Mo–C(5) 2.31(2)	C(6)–C(7) 1.44(2)	C(16)–C(17) 1.60(2)
Mo–C(6) 2.34(1)	C(8)–C(9) 1.47(2)	C(16)–C(23) 1.56(2)
Mo–C(7) 2.33(1)	C(5)–C(12) 1.54(2)	C(17)–C(18) 1.57(2)
Mo–C(8) 2.39(1)	C(8)–C(10) 1.48(2)	C(17)–C(21) 1.60(2)
Mo–C(9) 2.39(2)	C(9)–C(11) 1.50(2)	C(17)–C(22) 1.56(2)
C(1)–O(1) 1.18(2)	C(7)–C(13) 1.50(2)	C(18)–C(19) 1.52(2)
C(2)–O(2) 1.17(2)	C(6)–C(14) 1.48(2)	C(18)–C(23) 1.56(2)

Correspondence to: Dr. A. Heumann or Dr. R. Lai.

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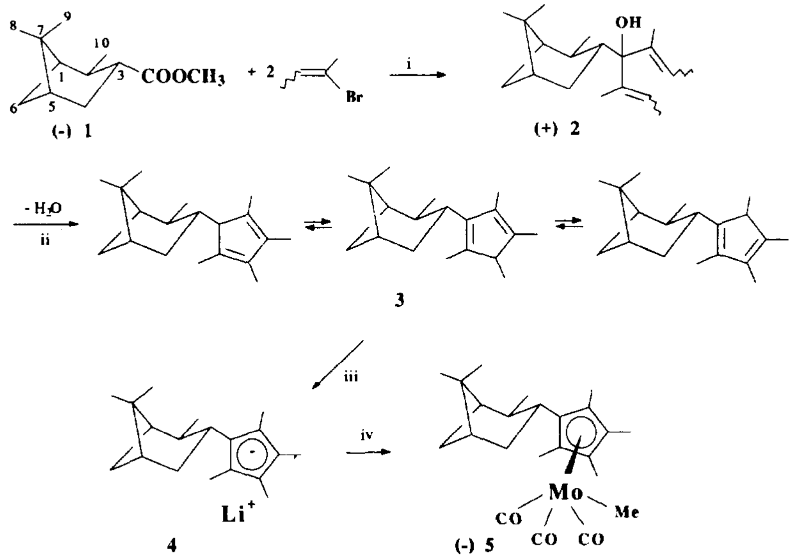

Scheme 1. *Reagents and conditions:* (i) Li, Et_2O, aq. NH_4Cl; (ii) $CuSO_4$–SiO_2, CCl_2=CCl_2; (iii) Ar, Li^{n}Bu, THF, 12 h reflux; (iv) $Mo(CO)_6$, THF, 12 h, reflux, MeI.

TABLE 2. Selected bond angles (°) for **5**

Mo–C(1)–O(1) 176(1)	C(6)–C(7)–C(13) 128(1)	C(14)–C(19)–C(18) 114(1)
Mo–C(2)–O(2) 177(2)	C(8)–C(7)–C(13) 123(1)	C(15)–C(16)–C(23) 108(1)
Mo–C(3)–O(3) 153(3)	C(7)–C(8)–C(10) 129(1)	C(15)–C(16)–C(17) 113(1)
C(1)–Mo–C(2) 79.5(7)	C(9)–C(8)–C(10) 125(1)	C(19)–C(18)–C(23) 108(1)
C(1)–Mo–C(3) 117.3(9)	C(5)–C(9)–C(11) 129(1)	C(19)–C(18)–C(17) 114(1)
C(1)–Mo–C(4) 73.3(8)	C(8)–C(9)–C(11) 124(1)	C(23)–C(18)–C(17) 85(1)
C(5)–C(6)–C(7) 105(1)	C(6)–C(5)–C(12) 127(1)	C(23)–C(16)–C(17) 84(1)
C(6)–C(7)–C(8) 109(1)	C(9)–C(5)–C(12) 120(1)	C(18)–C(23)–C(16) 89(1)
C(7)–C(8)–C(9) 106(1)	C(6)–C(14)–C(15) 109(1)	C(18)–C(17)–C(21) 118(1)
C(8)–C(9)–C(5) 106(1)	C(6)–C(14)–C(19) 117(1)	C(18)–C(17)–C(22) 113(1)
C(9)–C(5)–C(6) 113(1)	C(14)–C(15)–C(20) 112(1)	C(16)–C(17)–C(21) 122(1)
C(5)–C(6)–C(14) 131(1)	C(14)–C(15)–C(16) 113(1)	C(16)–C(17)–C(22) 112(1)
C(7)–C(6)–C(14) 123(1)		

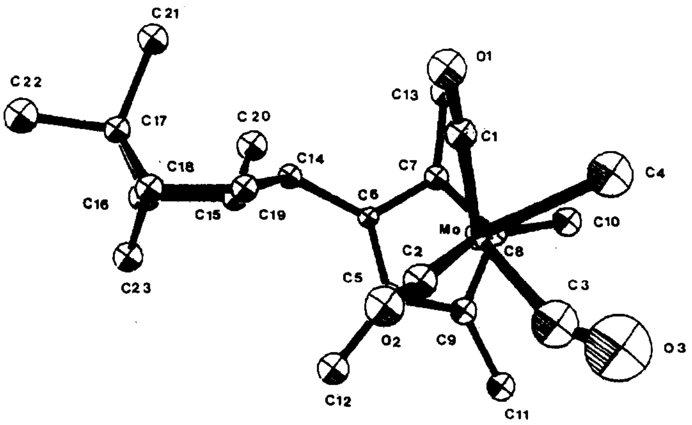

Fig. 1. Molecular structure and atom labelling of (−)-[Mo(η^5-C_5Me_4-3-pinanyl)(CO)$_3$Me] **5**.

signed to the pinanyl ring are only slightly affected by complexation to the metal. All the quarternary C-atoms, including those of the four methyl groups on the cyclopentadienyl residue as well as the carbonyl groups give separate signals. This transmission of the disymmetry to the cyclopentadienyl ligand (diastereotopic methyl groups) in a transition metal complex promises well for eventual stoichiometric or catalytic activities combined with asymmetric induction. Although complex (−)-**5** may find applications as a chiral auxiliary in reactions involving molybdenum carbonyls [10], the reactivity of this new cyclopentadienyl ligand will also be studied with different transition metals.

The structure of **5** was confirmed by an X-ray structure analysis. Pale yellow crystals of **5** were obtained by cooling a petroleum ether solution to −20°C. The results of the X-ray diffraction study are summarized in Tables 1 and 2 and illustrated in Fig. 1.

A four-legged piano-stool structure typical of [$CpML_4$] complexes is observed. The dimensions of (−) **5** are normal. The cyclopentadienyl C–Mo distances range between 2.31 (2) and 2.39 (2) Å, with a mean value of 2.35 Å, the Mo–Cp centroid distance being 2.01 (2) Å. The C–C bond lengths in the five-membered ring average 1.42 (2) Å. The C–C (methyl) distances in the cyclopentadienyl ring show no significant deviations from their average values of 1.50 (2) Å and the C–C bond distance between C_6 and C_{14} in the pinanyl ring is 1.48 (2) Å. The Cp ring is planar with a mean deviation within the experimental error. C–C–C bond angles in the C5 ring are equal except for C(9)–C(5)–C(6) which is 3σ above the mean value. With exception of methyl C(13), all the substituents at Cp are slightly out of the plane of the five-membered ring, the C–C (methyl) and C–C (pinanyl) vectors lying, respectively 7 and 12° out of this plane. The carbon monoxide ligands C(1)–O(1) and C(2)–O(2) exhibit normal bond lengths and angles, whereas C(3)–O(3) is rather different. The most significant change concerns the Mo–C(3)–O(3) angle which is almost 23° smaller than those of the two other Mo–CO angles. This is due to the thermal motion observed for C(3)–O(3).

The internal parameters of the pinanyl substituent deserve no special mention, the C–C bond distances range from 1.52 (2) to 1.60 (2) Å with a mean value of 1.57 Å.

Natural as well as synthetic chiral carboxylic acids are an easily accessible pool of chiral starting materials, and this method should become a general and extremely valuable entry into asymmetric cyclopentadiene chemistry. This approach should be valid for chiral mono- di- and tri-cyclopentadienyl ligands provided the starting compound is a mono-, di- or tri-basic carboxylic acid.

2. Experimental details

^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-200 and AM-400X spectrometers, IR spectra on a FT-IR Nicolet MX-S instrument. All manipulations were carried out under purified N_2 or Ar by standard Schlenk techniques. THF, pentane, petroleum ether and diethyl ether were distilled under dinitrogen from sodium benzophenone ketyl. All other chemicals were used as received.

2.1. (−)-(1S,2S,3S,5R) Pinane-3-carboxylic acid methyl ester, 1.

18.5 g (0.101 mol) of (−)-(1S,2S,3S,5R) pinane-3-carboxylic acid were dissolved in anhydrous methanol (400 ml) and, after addition of 16g of Amberlyst 15, stirred at room temperature for 50 h. Filtration, followed by removal of MeOH *in vacuo* left a residue which was extracted with hexane (2 × 150 ml). The combined organic phases were successively washed with a diluted solution of $NaHCO_3$ (2 ×) and water until neutral. The solution was dried over $MgSO_4$, filtered and evaporated to yield 17.6 g (88%) of **1**, after distillation at 63°C (0.8 mm Hg). ^{1}H NMR spectrum (400 MHz): δ 3.63 (s, 3H, OMe), 2.60 (d, t, J = 11 and 7 Hz, 1H), 2.26 (m, $W/2$ = 16 Hz, 2H), 2.10–2.19 (m, part of AB, 1H), 2.0 (ddd, J = 13.6, 6.5 and 2.7 Hz, part of AB, 1H), 1.87 (asymmetrical septet, $W/2$ = 12 Hz, 1H), 1.74 (poorly resolved td, J = 5.7 and 2 Hz, 1H), 1.15 (s, 3H), 1.05 (d, J = 7.2 Hz, 3H), 0.94 (s, 3H), 0.91 ppm (d, J = 9.8 Hz, 1H). ^{13}C NMR (100.52 MHz): δ 178.16 (CO), 51.73 (CH), 47.30 (CH), 41.79 (CH), 40.76 (CH), 39.61 (CH), 38.32 (C_{quart}), 33.16 (CH_2), 30.42 (CH_2), 27.96 (CH_3), 22.89 (CH_3), 22.09 ppm (CH_3). $[\alpha]_D^{22}$ (−) 29.40 ± 0.03 (c = 7.25, CH_2Cl_2).

2.2. (−)-[Mo(η^5-C_5Me_4-3-pinanyl)$(CO)_3$Me], 5

17.4 g (89 mmol) of **1** was added slowly to the lithium derivative of *cis/trans* (15/85 according to ^{1}H-NMR spectroscopy) 2-bromobut-2-ene (180 mmol) following very closely the procedure of Bercaw [5]. After work up, 24 g (98%) of crude tertiary dienyl alcohols **2** were isolated; $[\alpha]_D$ (+) 45.33 ± 0.3 (c = 18.95, CH_2Cl_2). For the dehydration, 4 g (14.5 mmol) of **2** were treated with 7.2 g of $CuSO_4$–SiO_2 [8] in tetrachloroethylene (70 ml) at 20°C during 1 h. The reaction mixture was filtered through Celite, and the Celite washed with ether. After evaporation of the solvents, the residue was purified by chromatography on silica gel (elution with hexane) to give **3** 2.2 g; yield: 60%. A solution of **3** (2.2 g, 8.5 mmol) in THF (40 ml) was heated under reflux under argon in the presence of 5.3 ml (8.5 mmol) Li^{n}Bu (1.6 M in hexane) for 8 h. After evaporation and drying *in vacuo*, the residue was washed with dry pentane (3 × 20 ml) and 1.6 g (71%) of the white solid **4** was obtained. The lithium salt **4** was immediately transformed into the molybdenum complex **5**. 0.86 g (3.3 mmol) **4** and 0.82 g (3.1 mmol) $Mo(CO)_6$ were heated under reflux in THF (25 ml) for 14 h. After cooling, 0.2 ml (3.3 mmol) of iodomethane were added and the solution stirred for 1 h at reflux and 1 h at room temperature. The solvent was pumped off and the brown residue extracted with hexane. After filtration and concentration the yellow hexane solution was passed through a silica gel column. Elution with hexane and evaporation yielded pure **5**, 1.03 g (70%), yellow crystalline solid. IR (KBr pellet): νCO 2005, 1930, 1908 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 2.93 (q, 1 H, *J*, 9.4 Hz, 2-H), 2.35 (dtd, 1 H, *J*, 2.1, 6.2 and 9.7 Hz, 4-H_{endo}), 2.21 (dddd, 1 H, *J*, 2.1, 4.06, 10.1 and 14 Hz, 6-H_{endo}), 2.02–2.09 (m, 2 H, 5-H and 3-H), 1.83–1.96 (m, 2 H, 1-H and 6-H_{exo}), 1.17 (d, 1 H, *J*, 7-9 Hz, 4-H_{exo}), 1.99, 1.92, 1.89, 1.81 (4 s, 12 H, 4 CH_3 at Cp), 1.26, 1.16 (2 s, 6 H, gem di-CH_3), 0.98 (d, 3 H, *J*, 7.05 Hz, CH_3, C_{10}), 0.07 ppm (s, 3 H, Mo–CH_3). ^{13}C NMR (100.52 MHz, $CDCl_3$): δ 243.26, 229.08, 228.93 (3 × CO), 114.08, 107, 104.22, 103.18 (br), 102.78 (5 C_{quart}, Cp), 49.36 (C_1), 44.15 (br, C_3), 43,31 (C_5), 39.54 (C_7), 37.81 (C_6), 34.53 (C_4), 34.2 (C_2), 28.85 (C_8), 23.54 (C_9), 21.61 (C_{10}), 12.01, 11.96, 10.62, 10.10, (4 CH_3, Cp), −10.91 ppm (Mo–CH_3). $[\alpha]_D$ (−) 41.91 ± 0.3 (c = 10.61, CH_2Cl_2).

TABLE 3. Positional parameters and their estimated standard deviations for (−) **5**

Atom	x	y	z	B ($Å^2$) [a]
Mo	0.5504(2)	0.0828(1)	0.15178(5)	3.22(2)
C1	0.398(2)	0.166(1)	0.1026(7)	4.9(4) *
O1	0.311(2)	0.214(1)	0.0703(5)	7.4(3) *
C2	0.353(2)	−0.015(1)	0.1400(8)	5.7(4) *
O2	0.231(2)	−0.070(1)	0.1318(5)	7.3(3) *
C3	0.453(4)	0.048(2)	0.228(1)	11.2(7) *
O3	0.402(4)	0.070(2)	0.271(1)	22(1) *
C4	0.496(4)	0.247(2)	0.1981(9)	10.5(7) *
C5	0.761(2)	−0.043(1)	0.1287(6)	4.0(3) *
C6	0.751(2)	0.0250(9)	0.0833(5)	2.3(3) *
C7	0.812(2)	0.125(1)	0.1037(6)	3.2(3) *
C8	0.866(2)	0.115(1)	0.1607(6)	3.3(3) *
C9	0.831(2)	0.004(1)	0.1758(6)	3.9(3) *
C10	0.955(3)	0.194(1)	0.1970(6)	5.0(3) *
C11	0.887(2)	−0.045(1)	0.2299(6)	4.3(4) *
C12	0.729(2)	−0.163(1)	0.1279(7)	5.3(4) *
C13	0.834(2)	0.226(1)	0.0718(6)	4.6(4) *
C14	0.717(2)	0.004(1)	0.0237(6)	3.0(3) *
C15	0.886(2)	−0.057(1)	−0.0020(6)	3.5(3) *
C16	0.833(2)	−0.130(1)	−0.0510(7)	5.0(4) *
C17	0.674(2)	−0.084(1)	−0.0884(6)	3.5(3) *
C18	0.540(2)	−0.123(1)	−0.0422(6)	3.8(3) *
C19	0.530(2)	−0.049(1)	0.0080(6)	3.6(3) *
C20	1.040(3)	0.018(1)	−0.0180(7)	5.4(4) *
C21	0.665(2)	0.038(1)	−0.1064(7)	4.8(4) *
C22	0.652(2)	−0.144(1)	−0.1444(8)	6.0(4) *
C23	0.686(2)	−0.208(1)	−0.0295(6)	4.4(3) *

[a] Atoms marked with asterisks were refined isotropically.

2.3. X-ray data collection and structure solution of (−)-5

5 crystallized in the orthorhombic space group $P2_12_12_1$, with a = 7.439 (3), b = 12.685 (5), c = 24.04 (1) Å; and V = 2268 $Å^3$; D_c = 1.313 g cm^{-3}; M_r = 452.17, Z = 4, μ = 5.83 cm^{-1}. A crystal of size 0.2 × 0.4 × 0.1 mm was protected by silicone oil and mounted on an Enraf–Nonius CAD4 diffractometer equipped with a monochromator for Mo K_α radiation (λ = 0.7107 Å), θ_{max} = 24°. 1203 unique reflections with $I > 3\sigma(I)$ were used in the structure determination. The structure was determined by direct methods (MULTAN) [11] using SDP software [12] and completed by the difference Fourier method. H-atoms were introduced at idealized positions in the calculation before the last refinement cycles but not refined. Full least-squares refinement included isotropic thermal parameters for all non H-atoms with the exception of molybdenum. A final difference Fourier synthesis did not reveal any peak of density > 0.35 e $Å^{-3}$. R = 0.056 and R_w = 0.069, $w = 1/\sigma^2$ (σ = estimated standard deviation of intensity). The non-hydrogen atom coordinates are listed in Table 3. Lists of H-atom coordinates, structure factors, and a complete table of bond lengths and angles are available from the authors.

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