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Synthesis and properties of optically active organomolybdenum compounds

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Abstract

The reaction of an optically active cyclopentadienyl salt, formed from the asymmetric reduction of 6-methyl-6-phenylfulvene, with $Mo(CO)_6$ followed by treatment with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, yields an optically active organomolybdenum complex. Thermally induced substitution of a carbon monoxide ligand by trimethyl- or triphenylphosphine produces products with two chiral centers.

Introduction

The use of organometallic complexes in organic synthesis and in particular in the area of asymmetric synthesis has recently been under extensive investigation. For example, chiral boranes [1] and titanium compounds [2] as well as asymmetric hydrogenations using chiral rhodium catalysts [3,4] have been increasingly used in the synthesis of novel organic molecules.

The potential for new chiral organometallic reagents depends heavily on the formation and availability of appropriate ligands. The most common ligand encountered in organotransition metal chemistry is the η^5-cyclopentadienyl moiety. Cyclopentadienyl-transition metal complexes have shown both stoichiometric and catalytic behavior toward a variety of substrates [5]. The literature abounds with examples of functionally substituted cyclopentadienylmetal compounds [6], however, fewer examples exist where the ring is substituted with chiral substituents [7]. In addition, to our knowledge only one example has been reported in which a chiral cyclopentadienyl ligand is bound to a molybdenum center [8]. In this paper, we report a synthetic route to several new optically active organomolybdenum compounds.

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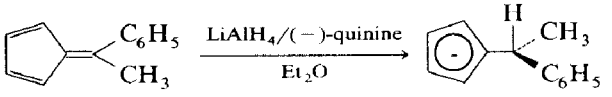
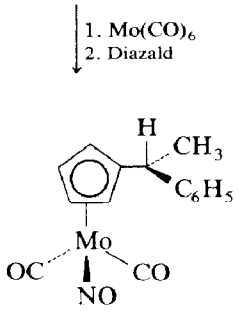
Results and discussion

The asymmetric reduction of 6-methyl-6-phenylfulvene by means of $LiAlH_4$/(−)-quinine in ethyl ether produced the optically active anion (**1**) with the *S* configuration [9]. The resulting anion was then allowed to react with $Mo(CO)_6$ in THF for 72 h at reflux, followed by treatment with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) [10] to yield (η^5-1-phenylethylcyclopentadienyl)dicarbonylnitrosylmolybdenum (**2**), $[\alpha]_D^{22} = +49.0°$ ($c = 0.003$, pentane) [*R* configuration] in 40% yield. The optical purity of **2** was not determined, however, related studies on anion **1** have demonstrated that it can be converted into a known ferrocene derivative of 32.3% optical purity.



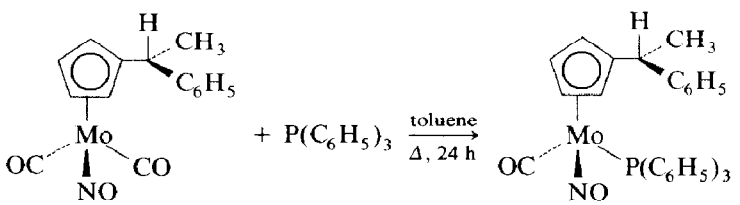
(**1**)



(**2**)

Compound **2** is a moderately air-sensitive dark red oil that is easily purified by column chromatography on 5% deactivated alumina. The ^1H NMR spectrum, taken in $CDCl_3$, exhibited a three-proton doublet at δ 1.45, assignable to the methyl protons, a one-proton quartet at δ 3.82, assignable to the methine proton, and other expected resonances. The IR spectrum showed the characteristic absorptions for a $CpMo(CO)_2NO$ compound and elemental analysis was also consistent with the proposed formulation.

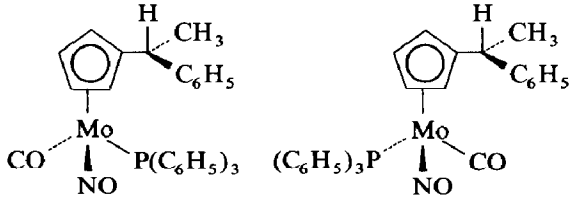
The thermolysis of **2** in benzene in the presence of 1.5 equivalents of triphenylphosphine failed to induce substitution of a carbon monoxide ligand. However, substitution could be accomplished by refluxing **2** in toluene with triphenylphosphine for 24 h. (η^5-1-Phenylethylcyclopentadienyl)carbonylnitrosyltriphenylphosphinemolybdenum (**3**) was isolated in 70% yield following chromatography.



(**2**) (**3**)

The NMR spectrum, taken in $CDCl_3$, exhibited a pair of doublets at δ 1.39 and δ 1.53, assignable to the methyl protons, as well as other characteristic resonances. The IR spectrum and elemental analysis were consistent with the proposed structure.

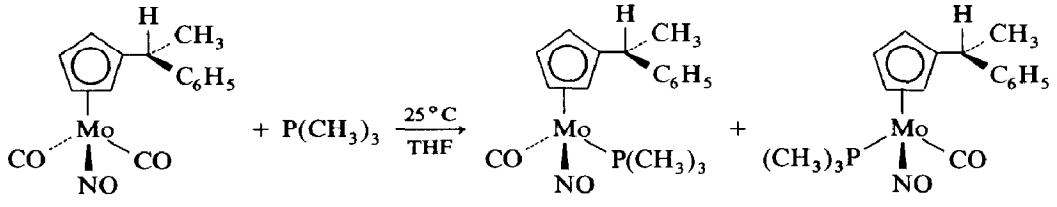
The doublets at δ 1.39 and δ 1.53 indicated the formation of a diastereomeric mixture. Substitution of a carbonyl ligand with a phosphine generates a chiral metal center and produces R,R and R,S configurations. Integration indicated a 50/50



(3 [R,S]) (3 [R,R])

mixture of the diastereomers **3** [R,S] and **3** [R,R]. Repeated attempts to separate the mixture by fractional recrystallization or by column chromatography were unsuccessful.

The reaction of **2** with trimethylphosphine proceeded rapidly at room temperature (90% within 10–15 min) [11*]. (η^5-1-Phenylethylcyclopentadienyl)carbonylnitrosyltrimethylphosphinemolybdenum (**4**) was isolated in 73% yield as a dark red liquid.



(4 [R,S]) (4 [R,R])

The ^1H NMR spectrum, taken in $CDCl_3$, exhibited a pair of doublets at δ 1.43 and δ 1.58, assignable to the methyl protons. As found with triphenylphosphine substitution of a carbonyl ligand, reaction of **2** likewise yielded a diastereomeric mixture. Integration again indicated a 50/50 mixture of the two diastereomers, and separation attempts as for **3** were not successful.

The reaction difference between the substituted and unsubstituted η^5-cyclopentadienyl rings illustrates the steric requirements expressed by the 1-phenylethyl group. The thermolysis of $CpMo(CO)_2NO$ in benzene with triphenylphosphine for 3 h resulted in a facile substitution reaction, while the reaction of $CpMo(CO)_2NO$ with $P(CH_3)_3$ proceeded rapidly even at low temperatures ($-60\,^\circ C$) [12]. Placing the 1-phenylethyl group on the η^5-cyclopentadienyl ring results in a decrease in reactivity due to a steric interaction between the chiral substitutent and the incoming phosphine.

* Reference number with asterisk indicates a note in the list of references.

Experimental

All operations were carried out utilizing standard Schlenk and vacuum line techniques under an argon atmosphere. Argon and solvents were purified as previously described [13]. Column chromatography was carried out using CAMAG neutral alumina. The alumina was predried in a 60 °C oven for 12 h, and then dried with a heat gun while mixing on a rotary evaporator attached to a vacuum pump for 2 h. The alumina was subsequently deactivated with water (5% by weight) which had been distilled under argon. Proton NMR spectra were recorded on Varian A-60 and 300 MHz spectrometers. IR spectra were recorded on a Perkin–Elmer 237B spectrophotometer. Molybdenum hexacarbonyl was obtained from Strem Chemical Co and used as obtained.

Preparation of 6-methyl-6-phenylfulvene

To a solution of 5 g of sodium metal in 75 ml of absolute ethanol was added slowly a mixture of 24 g (0.2 mole) of acetophenone and 13.2 g (0.2 mole) of freshly distilled cylopentadiene while maintaining the solution at 0 °C. After stirring for 12 h at 0 °C, the red solution was poured into 250 ml of water and methylene chloride was added. The organic layer was separated, washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure at room temperature. The resulting red oil was fractionally distilled through a short Vigreux column and the fraction boiling at 70 °C/0.10 mmHg was retained; yield 25 g (74%). Lit. b.p. 85–90 °C/0.5 mmHg [14].

Preparation of R-(+)-(η^5-1-phenylethylcyclopentadienyl)dicarbonylnitrosylmolybdenum (2)

Lithium aluminium hydride (0.45 g, 0.012 mole) was slurried in dry ethyl ether and cooled to 0 °C. (−)-Quinine (3.89 g, 0.012 mole) dissolved in 30 ml of dry ethyl ether was added over a 30 min period. The solution was then allowed to warm to room temperature and stirred for 2 h. 6-Methyl-6-phenylfulvene (2.00 g, 0.012 mole) dissolved in 20 ml of dry ethyl ether was added at room temperature and the mixture was stirred for 12 h.

The ethyl ether was removed under reduced pressure and the residue was taken up in dry tetrahydrofuran. Molybdenum hexacarbonyl (3.17 g, 0.012 mole) was added and the reaction mixture was refluxed for 72 h. The solution was cooled to room temperature and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (2.36 g, 0.01 mole) was added slowly with continuous stirring. The reaction mixture was stirred for 2 h. The tetrahydrofuran was removed under reduced pressure and the resulting residue was extracted with 400 ml of pentane. The pentane extracts were evaporated onto alumina and the resulting mixture was added to a prepacked column of alumina (15 × 1.5 cm). Elution with pentane produced an orange band which was collected under argon. The solvent was removed under reduced pressure yielding 2.0 g (48%) of (η^5-1-phenylethylcyclopentadienyl)dicarbonylnitrosylmolybdenum as a dark red oil. An analytical sample was obtained by molecular distillation. ^{1}H NMR ($CDCl_3$) δ 1.45 (3H, d, CH_3); 3.82 (1H, q, CH); 5.25-5.64 (4H, m, C_5H_4); 7.25 (5H, s, C_6H_5). IR (neat) 2010s, 1940s, 1660s cm^{-1}. Found: C, 51.20; H, 3.74; N, 4.26. $C_{15}H_{13}MoNO_3$ calc: C, 51.30; H, 3.73; N, 3.99%. $[\alpha]_D^{22} = +49.0°$ ($c = 0.003$, pentane).

Preparation of (η^5-1-phenylethylcyclopentadienyl)carbonylnitrosyltriphenylphosphinemolybdenum (3)

In dry toluene was dissolved *R*-(+)-(η^5-1-phenylethylcyclopentadienyl)dicarbonylnitrosylmolybdenum (0.77 g, 0.002 mole) and triphenylphosphine (0.75 g, 0.003 mole). The solution was then heated to reflux for 24 h. The mixture was cooled to room temperature and ca. 1 g of alumina was added. The solvent was removed under reduced pressure and the resulting residue was added to a prepacked column of alumina (15 × 1.5 cm). Elution of the column with pentane separated a small orange band which was not collected. The column was then eluted with benzene, yielding a dark red band which was collected under argon. The solvent was removed under reduced pressure, producing 0.90 g (70%) of (η^5-1-phenylethylcyclopentadienyl)carbonylnitrosyltriphenylphosphinemolybdenum as a dark red oil. An analytical sample was obtained by recrystallization from methylene chloride/hexane as dark red crystals. ^{1}H NMR ($CDCl_3$) δ 1.39, 1.53 (3H, dd, CH_3); 3.56–3.88 (1H, m, CH); 4.44–4.57 (4H, m, C_5H_4); 6.90–7.73 (20H, m, C_6H_5). IR (toluene) 1910s, 1605s cm^{-1}. Found: C, 65.37; H, 4.82; N, 2.30. $C_{32}H_{28}MoNO_2P$ calc: C, 65.64; H, 4.82; N, 2.39%.

Preparation of (η^5-1-phenylethylcyclopentadienyl)carbonylnitrosyltrimethylphosphinemolybdenum (4)

In dry tetrahdyrofuran was dissolved (η^5-1-phenylethylcyclopentadienyl)dicarbonylnitrosylmolybdenum (0.55 g, 0.002 mole). Trimethylphosphine (0.12 g, 0.002 mole) was added via syringe at room temperature. The reaction mixture turned from orange to dark red within 5 min after the addition of the phosphine. The solution was stirred at room temperature for 12 h. Alumina was added to the solution and the solvent removed under reduced pressure. The resulting residue was added to a prepacked column of alumina (15 × 1.5 cm). Elution with pentane failed to separate any bands. Further elution with benzene produced a dark red band which was collected under argon. The solvent was removed under vacuum leaving 0.47 g (73%) of a dark red oil. An analytical sample of (η^5-1-phenylethylcyclopentadienyl)carbonylnitrosyltrimethylphosphinemolybdenum was obtained by molecular distillation. ^{1}H NMR ($CDCl_3$) δ 1.43, 1.58 (3H, dd, CH_3); 1.41 (9H, d, $P(CH_3)_3$); 3.70 (1H, m, CH); 5.28 (4H, m, C_5H_4); 7.26 (5H, s, C_6H_5). IR (toluene) 1902s, 1607s cm^{-1}. Found: C, 50.98; H, 5.54; N, 3.70. $C_{17}H_{22}MoNO_2P$ calc: C, 51.14; H, 5.55; N, 3.51%.

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