DALTON

Ultrasound-promoted selective formation of optically active cyclopentadienyl ligands†

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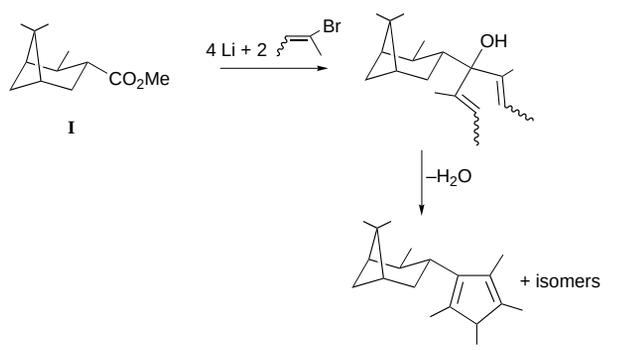
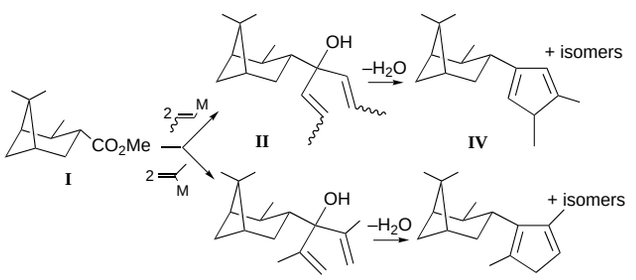
In order to prepare optically active cyclopentadienyl ligands, the chiral version of Bercaw's synthesis of 1,2,3,4,5-pentamethylcyclopentadiene was carried out between the Grignard- or the lithium-derivatives of 1- or 2-bromopropene and the methyl ester of (−)-pinane-3-carboxylic acid **I**. Under conventional conditions, the condensation of the vinylic Grignard reagents with **I** yielded, as the major products, the unsaturated ketones **VI** and **VII** (resulting from 1,4 addition to the intermediate vinylic ketones **VIII** and **IX**) instead of the expected dienic alcohols **II** and **III**. In the case of the lithium derivatives, obtained by halogen–metal exchange between LiBu^t and 1- or 2-bromopropene, the same reaction gives a better selectivity towards 1,2 addition. However, the reactions are rather tedious and a large excess of reactants is needed to achieve a total reaction. When a one-pot reaction was conducted under ultrasound irradiation with lithium wire, 1- or 2-bromopropene and **I**, the dienic alcohols, resulting from 1,2 addition to **VIII** and **IX** are the major products. Furthermore, under these conditions, addition of LiBr affords **II** and **III** almost quantitatively. Dehydration of **II** or **III** gives optically active trisubstituted cyclopentadienes **IV** or **V** as mixtures of isomers. Single-crystal X-ray structures of the corresponding cyclopentadienyl molybdenum complexes **1** and **2** have been determined.

It has been shown that optically active peralkylcyclopentadienyl ligands can be easily obtained by the chiral version[1] of Bercaw's reaction.[2] Using the same procedure (see Scheme 1) from the methyl ester of (−)-pinane-3-carboxylic acid **I** and the lithium derivatives of 2-bromo-2-butenes (*cis–trans* mixture), we have prepared in good yield the corresponding terpenylcyclopentadiene as a mixture of doubly bonded isomers.[3]

In the framework of our ongoing research on the synthesis and reactivity of new chiral cyclopentadienyl metal complexes, we thought it would be of interest to compare the influence of the substituent on the cyclopentadienyl unit on the performance of these complexes as chiral auxiliaries. We thus decided to perform the condensation of the vinylic organometallic species derived from 1- or 2-bromopropene with **I** to obtain chiral cyclopentadienes **IV** and **V**, according to Scheme 2.



Scheme 1



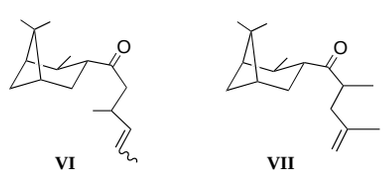
Scheme 2 M = Li or MgBr

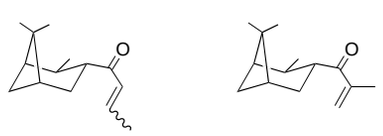
Results

Since the transformation of vinylic bromides to the corresponding lithio derivatives is usually difficult, we treated the Grignard reagents of either 1- or 2-bromopropene with **I** in tetrahydrofuran (thf). As shown in Table 1 (entries 1 and 2), the major products of the reaction are not the expected dienic alcohols **II** and **III** but the unsaturated ketones **VI** and **VII** arising from a 1,4 addition process to the intermediate vinylic ketones **VIII** and **IX**.

These results are in sharp contrast to those found in the condensation reaction involving the lithium derivatives formed from 2-bromo-2-butenes with esters.[1–3] In this case, indeed, 1,2 addition is the only reaction that occurs.

As it was not possible to obtain the vinylic lithium compounds from commercially available 1- and 2-bromopropene by conventional lithium metal methods, we then tried to react **I** with propenyllithiums prepared by halogen–metal exchange between 1- or 2-bromopropene and LiBu^t.[4,5] Under these conditions, 1,2 addition is predominant with respect to 1,4 addition. However, the reaction is not complete even after 12 h at room





† This paper is dedicated to the memory of Professor Sir Geoffrey Wilkinson.

Table 1 Condensation reactions of vinylic Grignard and lithium reagents on compound **I**

Entry	Vinyl bromide	Metallation reagent	Ultrasound employed?	Conversion (%)	Products[a] (%) II	III	VI	VII	Reaction time/h
1	1-Bromopropene	Mg turnings	No	70	22		48		1.5
2	2-Bromopropene	Mg turnings	No	78		1		77	1.5
3[b]	1-Bromopropene	LiBu^t	No	62	42				12
4[c]	2-Bromopropene	LiBu^t	No	100		75			3.5
5	1-Bromopropene	Li wire	Yes	100	78		22		4.5
6	2-Bromopropene	Li wire	Yes	100		67		33	6
7[d]	1-Bromopropene	Li wire	Yes	99	90.5		8.5		4
8[e]	1-Bromopropene	Li wire	Yes	100	99.5		0.5		2.5
9[d]	2-Bromopropene	Li wire	Yes	100		77		23	4
10[e]	2-Bromopropene	Li wire	Yes	100		79.5		20.5	2.5
11[f]	2-Bromopropene	Li wire	Yes	100		98		2	2.5

[a] Yields determined by GC. [b] Ratio **I**–1-bromopropene–LiBu^t = 1 : 2.3 : 3.8; 20% of Wurtz coupling products and unidentified side-products. [c] Ratio **I**–1-bromopropene–LiBu^t = 1 : 4 : 8; 25% of Wurtz coupling products. [d] Ratio **I**–LiBr = 1 : 2. [e] Ratio **I**–LiBr = 1 : 4. [f] Ratio **I**–LiBr = 1 : 8.

temperature. An excess of bromopropenes and LiBu^t is necessary to reach a complete transformation of **I** and, under these conditions, side-products such as Wurtz coupling hydrocarbons are detected in large amounts and the results are sometimes erratic and irreproducible (Table 1, entries 3 and 4).

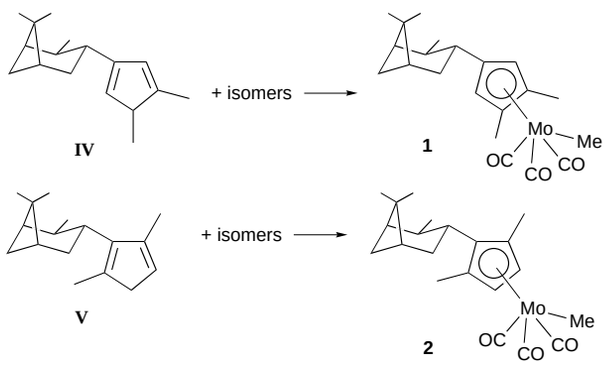
Some years ago it was found that ultrasonic irradiation affords a significant improvement in the generation of lithium organometallics.[6] We indeed observed that a fast reaction occurred when either 1- or 2-bromopropene was reacted in thf with lithium wire immersed in the water bath of an ultrasound apparatus. However, under these conditions, the obtained organolithium derivatives were not stable due to the intervention of highly favoured Wurtz coupling.[7,8] As the superiority of the ultrasound irradiation is strikingly evidenced in the Barbier reaction, in which a one-step coupling of an organic halide with a carbonyl compound is achieved with magnesium, or even better with lithium, we thought that a Barbier-type procedure would seem appropriate in our case, since formation of the lithium derivative occurs in the presence of the acceptor molecule.

Gratifyingly, we observed that the dienic alcohols could be synthesized with good selectivity in good yields by changing the experimental procedure. Indeed, when either 1- or 2-bromopropene was reacted under sonication with lithium metal in thf in the presence of the optically active methyl ester **I**, the reaction was complete within a few hours and gas chromatographic (GC) analysis of the reaction mixture showed that the major products were the dienic alcohols **II** and **III** (Table 1, entries 5 and 6). In the sonochemical runs, addition of excess LiBr afforded **II** and **III** in almost quantitative yields. This is in perfect accordance with the theory which predicts that the addition of salts influences the rate and the regioselectivity of nucleophilic addition to α,β-unsaturated compounds[9,10] (Table 1, entries 7–11).

We also observed that, under sonication conditions, when magnesium is used instead of lithium, 1,2 addition *versus* 1,4 addition is more important than it is under non-ultrasound conditions. However, in this case, the conversion is very low even after 10 h of reaction (less than 40% conversion). This lack of reactivity of magnesium compared to lithium could be due to some passivation of the metal.[11,12]

It has reported in the literature[13,14] that, under sonication, alkyllithiums react with α,β-unsaturated carbonyl compounds to give 1,2 addition products. However, to our knowledge, there are no examples of sonochemically induced reactions of vinylic lithium with α,β-unsaturated carbonyl compounds. Under these conditions, only reactions of vinylic organocopper or organozinc compounds have been described and they exclusively afford β-alkylated ketones resulting from 1,4 addition.[13–15]

The dienic alcohols **II** and **III**, as well as the β-alkylated unsaturated ketones **VI** and **VII**, have been characterized by



Scheme 3

one- and two-dimensional NMR spectroscopy, gas chromatography–mass spectrometry (GC/MS) and –infrared (GC/IR) analyses. Compounds **II** and **VI** are obtained as mixtures of geometrical isomers whereas **III** and **VII** are formed as single isomers.

The trisubstituted cyclopentadienes **IV** and **V** formed upon dehydration of **II** and **III** respectively by $NaHSO_4$ on silica[16] are isolated as mixtures of doubly bonded isomers in 75 and 35% yield, respectively, after purification by column chromatography and distillation under reduced pressure (these yields have been by no means optimized). Owing to the double-bond tautomerism of the cyclopentadiene unit, the NMR spectroscopy does not give reasonable structural information and the ligands were characterized after transformation into the molybdenum complexes **1** and **2**[17] (Scheme 3).

After purification on a column of silica, compounds **1** (30% yield) and **2** (25% yield) have been unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopy, and their structure confirmed by X-ray crystallography.‡

Complexes **1** and **2** are now being used as chiral auxiliaries in enantioselective allylic alkylation reactions and other complexes with different transition metals will be synthesized from the chiral cyclopentadienes **IV** and **V**.

Experimental

General

Preparations involving oxygen- or water-sensitive materials

‡ The absolute configuration of **1** and **2** is deduced by reference to the starting compound **I** since their formation does not involve the chiral part of **I**. The X-ray analyses confirm the structures of **1** and **2** as well as the stereochemical integrity of the carbon atom attached to the cyclopentadienyl units. However, due to the poor quality of the crystallographic data the structures will not be published but are available on request (CCDC reference number 186/646).

were carried out using standard glovebox and Schlenk techniques. Where necessary, solvents were distilled under argon over standard drying agents and were deoxygenated prior to use by the passage of a stream of argon. All reactions were conducted under an atmosphere of nitrogen or argon. Infrared spectra were recorded on a Perkin-Elmer Model 1720X spectrophotometer interfaced to a computer, using KBr pellets (4000–400 cm^{-1} scale). All NMR spectra were recorded on a Bruker AMX-400 instrument in $CDCl_3$ solutions at room temperature. The ^1H and ^{13}C chemical shifts of the solvent were used as a secondary reference and referenced to the $SiMe_4$ signal.[18] The complete ^1H and ^{13}C chemical shift assignment was performed using a concerted application of homonuclear (COSY[19]) and direct (HMQC[20]) inverse-detected heteronuclear correlation spectroscopy. Standard Bruker pulse sequences were used for the two-dimensional experiments. Further experimental details are given elsewhere.[21] Optical rotations for compounds **III** and **1** were measured on a Perkin-Elmer Model 241 digital polarimeter using a 1 dm cell length equipped with a thermostated water bath, and for compound **2**, on a Perkin-Elmer Model 241 MC digital polarimeter operating at 20 °C using a 1 dm cell length, the concentration *c* is given in g per 100 cm^3. Dichloromethane used for optical rotations was distilled and dried over P_2O_5 under argon, degassed and saturated with argon prior to use. Elemental analyses were performed by the 'Service Commun de Microanalyse' (Faculté de St Jérôme à Marseille). The GC/MS analyses were performed on a Ribernag R-10.10C apparatus and GC/IR analyses were run on an IR Fourier-transform Nicolet 20SXB spectrophotometer interfaced to a Carlo Erba Mega HRGC 5300 chromatograph at 'Service de Spectrophotométrie' (Faculté de St Jérôme à Marseille).

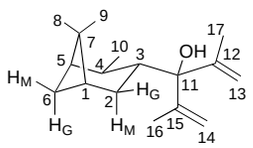
Preparations

The methyl ester of (−)-pinane-3-carboxylic acid **I** was prepared as previously described[3] and 1-bromopropene (*cis–trans* mixture) and 2-bromopropene from Aldrich were passed through a short column of basic alumina before use.

Reactions with Grignard reagents. A typical preparation was as follows. Under nitrogen, to preactivated magnesium turnings (1.0 g, 41.1 mmol) covered with thf (5 cm^3) were added a few drops of a solution of 2-bromopropene (4.35 g, 35.9 mmol) in thf (40 cm^3). Once the reaction had started the remaining solution was added slowly and at the end of the addition, **I** (3.60 g, 18.3 mmol) was added dropwise. The reaction mixture was then refluxed for 1 h and allowed to cool to room temperature. A saturated solution of NH_4Cl (45 cm^3) was added and the organic layer separated. The resulting aqueous layer was extracted with Et_2O (4 × 50 cm^3). The combined organic fractions were dried over $MgSO_4$ and the solvents removed *in vacuo* to give 4.42 g of crude product which was analysed by gas chromatography.

Reactions with organolithiums. (*a*) *By halogen–metal exchange.* A typical experiment was as follows. Under argon, 2-bromopropene (5.32 g, 44 mmol) was introduced in a two-necked flask in thf (75 cm^3). To this solution, cooled to −78 °C, was added dropwise $LiBu^t$ (49.2 cm^3, 84 mmol; 1.7 M in pentane). The solution was stirred for 1.5 h and then, at this temperature, **I** (4.24 g, 21.6 mmol) was slowly added. After stirring overnight at room temperature, Et_2O (30 cm^3) and a saturated solution of NH_4Cl (50 cm^3) were added. The organic layer was separated off and the aqueous layer was washed with Et_2O (4 × 50 cm^3). The combined organic layers were dried over $MgSO_4$ and the solvents removed *in vacuo* to yield 4.50 g of crude product.

(*b*) *By ultrasound irradiation.* In a typical experiment, to lithium wire (0.51 g, 73.4 mmol) (Aldrich, 99.9% purity, 0.01% Na) cut into small pieces under argon in a two-necked flask equipped with a condenser, **I** (3.0 g, 15.3 mmol) in thf (150 cm^3) and 2-bromopropene (4.50 g, 37.2 mmol) were introduced under argon. The flask was immersed to the solvent level in the water bath of an ultrasound apparatus (Transonic TS 540, 35 kHz, 160 W). The irradiation was started which caused the temperature of the water bath to increase to 45–50 °C. Samples were periodically withdrawn, quenched with a saturated solution of NH_4Cl washed with Et_2O and analysed by gas chromatography. At the end of the reaction, a saturated solution of NH_4Cl (150 cm^3) was added. The organic layer was separated off and the aqueous layer was washed with Et_2O (3 × 50 cm^3). The combined organic layers were dried over $MgSO_4$ and the solvents removed *in vacuo* to yield 3.24 g of crude **III**. Purification by column chromatography on silica followed by microdistillation (68–72 °C; 0.76 × 10^{-3} Torr, 1 Torr = 133.322 Pa) afforded pure **III**, 1.70 g, 45% yield based on **I**. $[\alpha]_{24}^{546} = +23.98° \pm 0.21$ (*c* = 0.079, CH_2Cl_2). For this bicyclo-[3.1.1]heptane compound we used, to designate stereochemical relationships, the M/G (mit/gegen) system as previously described.[22] The NMR attribution was made according to the following numbering scheme:



^1H NMR (400 MHz, $CDCl_3$): δ 5.17 (1 H, d, 0.9) and 4.95 (1 H, t, 1.5) (H^{13} or H^{14}), 4.98 (1 H, t, 1.4) and 4.88 (1 H, s) (H^{14} or H^{13}), 2.36 (1 H, dt, 10.4, 6.0, H^3), 2.12 (1 H, dtd, 9.3, 6.1, 2.1, $H^6{}_M$), 2.05 (1 H, dddd, 14.0, 10.4, 3.1, 2.2, $H^2{}_G$), 1.91 (1 H, qntd, 6.94, 2.3, H^4), 1.84 (1 H, m, H^1), 1.69 (1 H, m, H^5), 1.69 (1 H, s, OH), 1.66 (1 H, ddd, 14.0, 5.8, 3.0, $H^2{}_M$), 1.66 (6 H, s, Me^{16} and Me^{17}), 1.16 (3 H, s, Me^9), 1.03 (1 H, d, 9.4, $H^6{}_G$), 1.00 (3 H, s, Me^8), 0.92 (3 H, d, 7.0, Me^{10}). ^{13}C-{^1H} NMR (100 MHz, $CDCl_3$): δ 147.2 (C^{12} or C^{15}), 146.5 (C^{15} or C^{12}), 112.6 (C^{13} or C^{14}), 111.6 (C^{14} or C^{13}), 83.2 (C^{11}), 49.0 (C^5), 41.6 (C^1), 39.2 (C^3), 38.8 (C^7), 36.7 (C^4), 31.2 (C^2 or C^6), 31.1 (C^6 or C^2), 27.6 (C^9), 23.4 (C^8 or C^{10}), 23.4 (C^{10} or C^8), 21.3 (C^{16} or C^{17}), 19.3 (C^{17} or C^{16}).

The isomeric dienic alcohols **II** were obtained by the same procedure in similar yields (103–104 °C; 0.75 × 10^{-3} Torr).

Dehydration reaction. A typical experiment was as follows. The dehydration catalyst was prepared according to a literature procedure.[16] Under nitrogen, to activated $NaHSO_4$–SiO_2 (2.68 g, 36% $NaHSO_4$, 8.06 mmol) was added **II** (2.0 g, 8.06 mmol) in CCl_4 (80 cm^3). The resulting suspension was stirred at 20 °C for 9 h. The reaction was monitored by gas chromatography. The reaction mixture was passed through a column of Celite, washed with CH_2Cl_2 and the solvents removed under reduced pressure yielding 2.0 g of crude product. Purification by chromatography on silica followed by microdistillation (86–88 °C; 0.2 Torr) yielded the isomeric trisubstituted cyclopentadienes **IV**, 1.40 g, 75% yield.

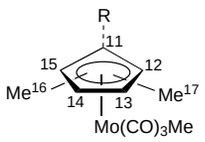
Trisubstituted cyclopentadienes **V** (83–88 °C; 0.45 Torr) were obtained from **III** in 35% yield, using the same procedure.

Optically active molybdenum complexes. Tricarbonyl(methyl)-[(+)-1-(3-pinanyl)-3,4-dimethylcyclopentadienyl]molybdenum **1** and tricarbonyl(methyl)[(−)-1-(3-pinanyl)-2,5-dimethylcyclopentadienyl]molybdenum **2** were prepared from isomeric **IV** and **V** according to a previously described procedure,[3] in 30 and 25% yields, respectively. For compound **1**: $[\alpha]_{32}^{546} = +8.72° \pm 0.32$ (*c* = 1.9, CH_2Cl_2); IR (cm^{-1}, KBr pellets): ν(CO) 2005vs, 1931 (sh) and 1913vs (Found: C, 59.5; H, 6.5. Calc. for $C_{21}H_{28}MoO_3$: C, 59.43; H, 6.65%).

For compound **2**: $[\alpha]_{20}^{651} = -42.6° \pm 1.7$ (*c* = 0.74, CH_2Cl_2); IR

(cm^{-1}, KBr pellets): ν(CO) 2012vs, 1916vs and 1904vs (Found: C, 59.3; H, 6.6. Calc. for $C_{21}H_{28}MoO_3$: C, 59.43; H, 6.65%).

The NMR attribution was made according to the following numbering scheme:



(R = 3-pinanyl, numbering scheme as described above)

For compound **1**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.99 (1 H, d, 2.1, H^{12} or H^{15}), 4.95 (1 H, d, 2.1, H^{15} or H^{12}), 2.41 (1 H, dt, 10.3, 7.0, H^3), 2.33 (1 H, dtd, 9.5, 6.3, 2.1, $H^6{}_M$), 2.21 (1 H, dddd, 13.6, 10.1, 3.6, 2.2, $H^2{}_G$), 1.94 (1 H, m, H^1), 1.86 (3 H, s, Me^{16} or Me^{17}), 1.79 (3 H, s, Me^{17} or Me^{16}), 1.77 (1 H, m, H^5), 1.74 (1 H, m, H^4), 1.54 (1 H, ddd, 13.8, 7.0, 2.5, $H^2{}_M$), 1.18 (3 H, s, Me^9), 1.05 (3 H, d, 7.1, Me^{10}), 0.99 (3 H, s, Me^8), 0.84 (1 H, d, 9.6, $H^6{}_G$), 0.17 (3 H, s, $MoCH_3$). ^{13}C-{^{1}H} NMR (100 MHz, $CDCl_3$): δ 241.9, 228.5, 228.3 (CO), 118.0 (C^{11}), 110.2 (C^{13} or C^{14}), 106.2 (C^{14} or C^{13}), 90.9 (C^{12} or C^{15}), 89.3 (C^{15} or C^{12}), 48.2 (C^5), 47.4 (C^4), 41.8 (C^1), 38.5 (C^7), 36.6 (C^3), 36.1 (C^2), 34.2 (C^6), 28.1 (C^9), 23.1 (C^8), 21.3 (C^{10}), 11.8 (C^{16} and C^{17}), −14.3 ($MoCH_3$).

For compound **2**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.94 (1 H, d, 2.8, H^{13} or H^{14}), 4.88 (1 H, d, 2.8, H^{14} or H^{13}), 2.92 (1 H, q, 9.6, H^3), 2.35 (1 H, dtd, 9.7, 6.2, 2.1, $H^6{}_M$), 2.21 (1 H, dddd, 13.6, 10.1, 4.0, 2.1, $H^2{}_G$), 2.09 (1 H, dqd, 9.3, 7.3, 1.5, H^4), 2.05 (1 H, m, H^1), 2.04 (3 H, s, Me^{16} or Me^{17}), 1.91 (3 H, s, Me^{17} or Me^{16}), 1.90 (1 H, ddd, 13.7, 8.9, 2.0, $H^2{}_M$), 1.85 (1 H, td, 5.6, 1.5, H^5), 1.24 (3 H, s, Me^9), 1.14 (3 H, s, Me^8), 1.13 (1 H, d, 8.3, $H^6{}_G$), 0.98 (3 H, d, 7.1, Me^{10}), 0.22 (3 H, s, $MoCH_3$). ^{13}C-{^{1}H} NMR (100 MHz, $CDCl_3$): δ 242.1, 227.8, 227.7 (CO), 118.0 (C^{11}), 108.2 (C^{12} or C^{15}), 107.0 (C^{15} or C^{12}), 92.0 (C^{13} or C^{14}), 88.3 (C^{14} or C^{13}), 49.4 (C^5), 43.9 (C^4), 43.2 (C^1), 39.5 (C^7), 37.5 (C^2), 34.6 (C^6), 34.0 (C^3), 28.8 (C^9), 23.6 (C^8), 21.6 (C^{10}), 14.6 (C^{16} or C^{17}), 14.0 (C^{17} or C^{16}), −14.4 ($MoCH_3$).

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