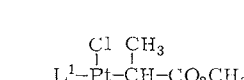
from the reaction medium by addition of diethyl ether. As a dry solid, complex **1** decomposes rapidly forming a mixture of products in which *cis*-$PtCl_2[P(OMe)_3]_2$ and $Pt[P(OMe)_3]_4$[4] can be identified from their ^{31}P-NMR parameters. However, solutions of compound **1** are stable at room temperature for several hours even in air.

Characterization of compound **1**[5] follows from its NMR spectra[6]. While the ^{1}H-NMR data of the hydrido ligand are very similar to those of *trans*-$PtHCl[PEt_3]_2$[7], the ^{31}P-NMR data are typical of $P(OR)_3$-complexes, i.e. low field δ^{31}P values and large $^1J_{P\text{-}Pt}$ values[8].

The thermally more stable **2** can be prepared similarly[9].

Compounds **1** and **2** react rapidly with $CH_2{=}CH{-}CO_2Me$ in acetone at room temperature to give the insertion products **3** and **4**, respectively.



3, $L^1 = L^2 = P(OMe)_3$[10]
4, $L^1 = L^2 = PMe(OMe)_2$[11]

There are three notable features to this insertion reaction:

1) It proceeds smoothly, even though chloride is coordinated to the platinum atom in contrast to *trans*-$PtHCl[PEt_3]_2$, which does not react with methyl acrylate[12].
2) Complexes **3** and **4** have the usual *cis*-geometry, but do not rearrange to their respective *trans*-isomers as found for the corresponding PEt_3-complexes[13].
3) Only a branched alkyl chain is formed, irrespective of the nature of solvent used for this reaction, in contrast to the behavior of the PEt_3-complexes where the branched is always accompanied by the linear isomer and the ratio of these two forms is solvent-dependent[14].

In summary, hydridoplatinum(II) complexes with phosphites or phosphonites can be obtained and show very high reactivity and regioselectivity towards alkene insertion. Thus, they could prove to be useful reagents and/or catalysts for organometallic reactions.

Received: February 28, 1984;
revised: May 3, 1984 [Z 728 IE]
German version: *Angew. Chem. 96* (1984) 505

CAS Registry numbers:
1, 90838-78-1; **2**, 90838-79-2; **3**, 90838-80-5; **4**, 90838-81-6; *cis*-$PtCl_2[P(OMe)_3]_2$ 28374-51-8; *cis*-$PtCl_2[PMe(OMe)_2]_2$ 90838-82-7

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[5] Although its easy decomposition prevented the determination of its elemental analysis, a determination of the Pt:P:Cl ratio gives the values 1:2.14:0.95. These elements were determined by X-ray fluorescence. The authors are indebted to Prof. *B. Magyar* and *B. Aeschlimann* for this determination.
[6] ^{1}H-NMR (90 MHz) in [D$_6$]acetone: $\delta(CH_3)=3.88$ (pseudotriplet), $|^3J_{P-H}+{}^5J_{P-H}|=14$ Hz; $\delta(PtH)=-16.34$, $^1J_{Pt-H}=1211$ Hz, $^2J_{P-H}=18$ Hz; $^{31}P\{^1H\}$-NMR (36.43 MHz, H_3PO_4 ext.), in [D$_6$]acetone: $\delta=126$, $^1J_{Pt-P}=4661$ Hz; $^{195}Pt\{^1H\}$-NMR: (53.53 MHz, K_2PtCl_6 ext. standard) in CD_2Cl_2: $\delta=-4956.5$ (t).
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[9] IR: $\nu(Pt-H)=2060$ cm^{-1}; ^{1}H-NMR (90 MHz) in benzene: $\delta(OCH_3)=3.62$ (pseudotriplet) $|^3J_{P-H}+{}^5J_{P-H}|=7$ Hz, $\delta(CH_3)=1.68-1.93$ (complex multiplet); $\delta(Pt-H)=-15.35$, $^1J_{Pt-H}=1255$ Hz, $^3J_{P-H}=9.4$ Hz; ^{31}P (36.43 MHz, H_3PO_4 ext. standard) in [D$_6$]acetone: $\delta=160$, $^1J_{Pt-P}=3673$ Hz; determination of the Pt:P:Cl ratio gives 1:1.95:1.04.
[10] IR: $\nu(C{=}O)=1740$ cm^{-1}, $\nu(Pt-Cl)=310$ cm^{-1}. ^{1}H-NMR (90 MHz) in CD_2Cl_2: $\delta(POCH_3)=3.70$, 3.80; $\delta(PtCHCH_3COOCH_3)=1.15$ (ddd), $^3J_{H-H}=7$ Hz, $^4J_{P2-H}=1$ Hz, $^4J_{P1-H}=14$ Hz, $^3J_{Pt-H}=16$ Hz; $\delta(PtCHCH_3COOCH_3)=3.50$ (s); $^{13}C\{^1H\}$-NMR (62.87 MHz) in CD_2Cl_2 (multiplicity of the resonances in an "off-resonance" mode are shown in parentheses): $\delta(PtCHCH_3COOCH_3)=28.79$ (t), $^1J_{C-Pt}=460.8$ Hz, $^2J_{C-P1}=4.7$, $^2J_{C-P2}=129.4$ Hz; $\delta(PtCHCH_3COOCH_3)=16.02$ (q), $^2J_{C-P}=7.4$ Hz, $^3J_{C-Pt}=22.2$ Hz; $\delta(PtCHCH_3COOCH_3)=50.23$ (q); $\delta(PtCHCH_3COOCH_3)=180.44$ (s), $^2J_{C-Pt}=42.0$ Hz, $^3J_{C-P}=6.7$ Hz. ^{31}P-NMR (36.43 MHz, H_3PO_4 ext. standard) in [D$_6$]acetone: $\delta(P_1)=119.3$, $^1J_{P1-Pt}=3068$ Hz; $\delta(P_2)=85.6$, $^1J_{P2-Pt}=6248$ Hz; $^2J_{P-P}=40$ Hz; determination of the Pt:P:Cl ratio gives 1:1.94:1.05.
[11] IR: $\nu(C{=}O)=1700$ cm^{-1}. ^{1}H-NMR (90 MHz) in CD_2Cl_2: $\delta(POCH_3)=3.43$, 3.61 (complex multiplet), $\delta(PtCHCH_3COOCH_3)=1.02$ (ddd), $^3J_{H-H}=6$ Hz, $^4J_{P2-H}=1$ Hz, $^4J_{P1-H}=9$ Hz, $^3J_{Pt-H}=15$ Hz; $\delta(PtCHCH_3COOCH_3)=3.34$ (s); $\delta(P_1-CH_3)=1.61$, $^2J_{P1-CH_3}=9$ Hz, $^3J_{Pt-P1CH_3}=3$ Hz; $\delta(P2-CH_3)=1.58$, $^2J_{P2-CH_3}=7$ Hz, $^3J_{Pt-P2CH_3}=9$ Hz; $^{13}C\{^1H\}$-NMR (62.87 MHz) in CD_2Cl_2: $\delta(PtCHCH_3COOCH_3)=28.31$, $^1J_{C-Pt}=458.4$ Hz, $^2J_{C-P1}=4.9$ Hz, $^2J_{C-P2}=108.5$ Hz; $\delta(PtCHCH_3COOCH_3)=15.9$, $^3J_{C-P}=6.0$ Hz (tentative assignment); $\delta(PtCHCH_3COOCH_3)=180.99$, $^2J_{C-Pt}=40.3$ Hz, $^3J_{C-P}=4.9$ Hz; $\delta(PtCHCH_3COOCH_3)=50.19$; ^{31}P-NMR (36.43 MHz, H_3PO_4) in [D$_6$]acetone: $\delta(P_1)=150$, $^1J_{P1-Pt}=2623$ Hz; $\delta(P_2)=117$, $^1J_{P2-Pt}=5540$ Hz; $^2J_{P-P}=27$ Hz; determination of the Pt:P:Cl ratio gives 1:1.98:1.02.
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Synthesis and Determination of the Absolute Configuration of (+)-Delesserine, a Metabolite of the Red Marine Alga *Delesseria sanguinea* (Lamouroux)

By *Dieter Seebach**, *Matthias Dust*, *Reto Naef*, and *Markus Bänziger*

Delesserine **6** is a γ-lactone isolated from the algae *Delesseria sanguinea* (Lamouroux). The relative configuration was determined by an X-ray crystal structure analysis[1], Aqueous extracts of *Delesseria sanguinea*, an alga occurring on the European Atlantic coast, are powerful anticoagulants for human blood[2].

We describe here a short synthesis of enantiomerically pure, natural delesserine **6** starting from diethyl (*R,R*)-(+)-tartarate[3] and demonstrate the relationship of delesserine to the (L)-series of C_6-carbohydrates, which had previously only been conjectured.

The key reaction in the synthesis is the addition of the lithium enolate of the phenyl lactic acid derivative **1** to the aldehyde **2** [acetonide and benzyl-protected (L)-threose], which was synthesized in four steps from diethyl tartarate[3-5]. Information about the formation of this C–C linkage, which completes the assembly of the carbon skeleton, and about further reactions is given in Scheme 1. Alcohol **3** (four diastereomers) was oxidized directly, without isolation, to the β-keto ester **4**, which was present in two forms epimeric at the α-C atom. After hydrolysis of the acetonides, a 1:2 mixture of lactones **5a** and **5b** was obtained, from which isomer **5a** could be isolated as ana-

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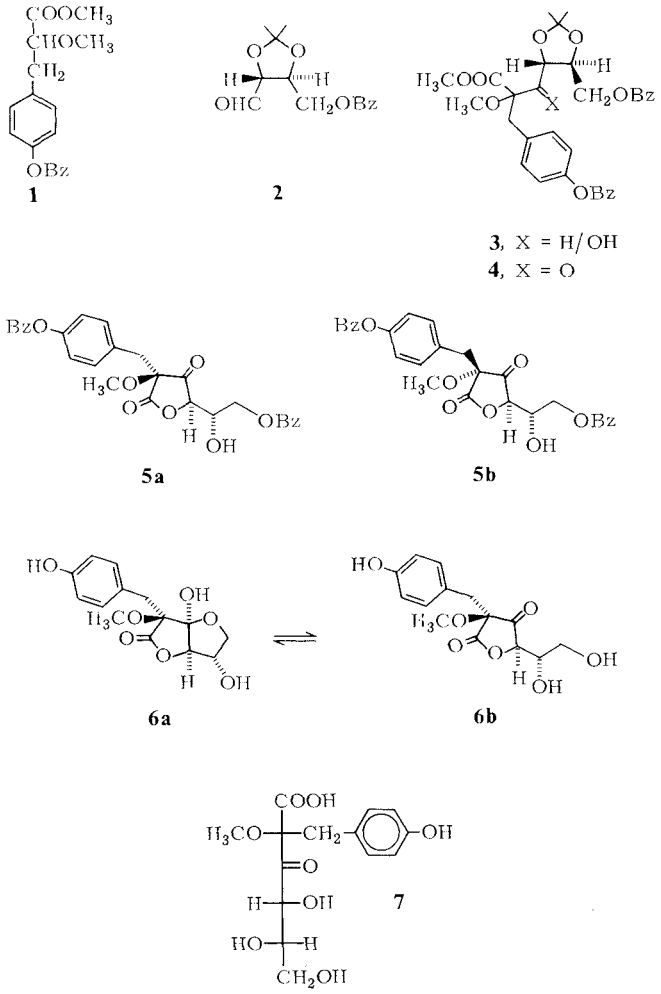
  0570-0833/84/0707-0530 $ 02.50/0

lytically pure crystals. After debenzylation of **5a** via hydrogenation, delesserine **6**, which exists in solution as an equilibrium mixture of the bicyclic and monocyclic forms



Scheme 1. Bz = benzyl. **1**: From methyl methoxyacetate and 4-benzyloxybenzyl bromide with lithium diisopropylamide (LDA) in tetrahydrofuran (THF), −75 °C, yield 86%.—**2**: In four steps from diethyl (+)-tartarate[4], 40%.—**3**: From **1** (LDA in THF, −75 °C) and **2**.—**4**: By Swern-oxidation [8] of **3** (dimethyl sulfoxide (DMSO), $(COCl)_2$, Et_3N, in CH_2Cl_2); 62% based on **2**.—**5**: By hydrolysis of the acetonide protecting group (TsOH, MeOH) 91%. Separation of the two diastereomers by crystallization from ether/pentane; **5a** (35% of the mixture) crystallized (m.p. 144 °C), **5b** (65% of the mixture) remains in the mother liquor and is isolated as an oil.—**6**: From **5a** by debenzylation with Pd/C in MeOH; 90% colorless, non-crystalline powder, m.p. ≈ 105 °C, $[\alpha]_D^{20} = +44$ ($c = 0.72$, MeOH) [6] (natural product: +36 [1]); ratio **6a/6b** (5 mg/mL CD_3OD): 63/37 (^{1}H-NMR); ^{13}C- and ^{1}H-NMR data of **6a** and **6b** agree with the values given in [1].

6a and **6b**, was obtained. The identity of **6** was proven by comparison of the sign and magnitude of its optical rotation and ^{1}H-NMR data with the values reported in the literature[1,6]. Delesserine **6** possesses no anticoagulant properties in the Quick test[7].

Received: March 12, 1984 [Z 756 IE]
German version: *Angew. Chem. 96* (1984) 498

CAS Registry numbers:
1, 74649-77-7; **2**, 81028-12-8; **3** (isomer 1), 90866-60-7; **3** (isomer 2), 90899-80-2; **3** (isomer 3), 90899-81-3; **3** (isomer 4), 90899-82-4; **4** (isomer 1), 90858-88-1; **4** (isomer 2), 90899-52-8; **5a**, 90858-89-2; **5b**, 90899-53-9; **6a**, 82198-78-5; **6b**, 90899-54-0; methyl methoxyacetate, 6290-49-9; 4-benzyloxybenzyl bromide, 5544-60-5

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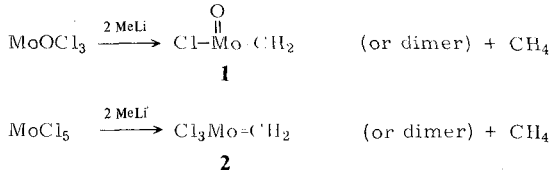
Carbonyl Olefinations with Methylenemolybdenum Reagents in Aqueous or Ethanolic Media**

By *Thomas Kauffmann*, Petra Fiegenbaum,* and *Raphael Wieschollek*

Among the known transition metal reagents that have been used for carbonyl olefinations[2,3], the molybdenum complexes first reported by us[2c,d] deserve special attention, since they are the most easily accessible and are comparable in their carbonyl selectivity to the titanium-containing alkylating reagents[4].

We report herein that the Mo-compounds **1** and **2** accessible according to Scheme 1 are—other than the titanium-containing Tebbe-reagent[2a] and the structurally related Zr-reagents of *Schwartz* et al.[2b]—suitable for carbonyl olefination in aqueous or ethanolic solvents[5], which could prove advantageous in the case of hydrophilic substrates.



Scheme 1.

The reagent prepared in anhydrous tetrahydrofuran (THF) (5 mmol in 50 mL) according to Scheme 1 is treated with the carbonyl compound dissolved or suspended in water, ethanol/water mixture, or ethanol (in each case ca. 20 mL) (Table 1). If this is carried out at −70 °C, the mixture is allowed to warm to room temperature within 12 h; if the addition is carried out at 0 °C, then the mixture is kept at this temperature for 1 h.

Reactions with **1**: The yields of alkene (Table 1) on addition of the substrate in ethanol or ethanol/water at −70 °C are practically the same as on addition of the substrate in anhydrous THF, with one exception: for some unknown reason **1** reacts better with benzaldehyde in the presence of water or ethanol. Thus, as a rule, the carbonyl olefination is more rapid than a replacement of the Cl substituents in **1** by OEt or OH. If, however, water is added at 0 °C there is a distinct loss in reactivity.

Reactions with **2**: In ethanol or aqueous THF the yields of alkene are substantially lower than in anhydrous THF (Table 1). The drastic reduction in yield of alkene on addi-

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[**] Transition Metal-Activated Organic Compounds, Part 15. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.—Part 14: [1].