

Oligomerization of Ethylene with Cationic Phenanthroline(methyl)palladium Complexes

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A number of cationic phenanthroline(methyl)palladium complexes, **3a–e**, have been generated in the presence of ethylene. The idea behind this design is twofold: (I) the presence of the phenanthroline ligand should prevent potential β -hydrogen elimination and (II) the cationic state of palladium decreases the stability of the bond between the alkene and the metal and will thereby facilitate migratory insertion of ethylene into the σ -carbon–palladium bond. In the absence of steric constraints at the phenanthroline ligand, these complexes catalyze the dimerization and oligomerizations of ethylene. General factors considered of importance for oligo- and poly-merization of alkenes are discussed.

The early transition metals and the lanthanides are well known as catalysts for the polymerization of simple alkenes. However, among the late transition metals those down the triads do not usually catalyze polymerization or oligomerization of simple alkenes.

There are some remarkable exceptions within this grouping. In 1967, Ketley noticed unexpected ethylene polymerization in the presence of solid palladium cyanide.¹ There is also a slightly earlier patent, referred to by Ketley, claiming palladium cyanide to polymerize ethylene.² In addition, Sen has reported that $(\text{CH}_3\text{CN})_4\text{Pd}^{2+}(\text{BF}_4)_2^-$, which as palladium cyanide is insoluble, can induce oligomerization beyond dimers of carboethylene by way of a carbocationic mechanism.³ Recently Flood discovered an extraordinary rhodium-catalyzed polymerization of ethylene.⁴ In addition, palladium- and rhodium-catalyzed copolymerizations of alkenes and carbon monoxide affording polyketones are well known.⁵ However, this is a rather different case since the polymerization consists of *alternating* migratory insertions: a carbon monoxide insertion into a σ -alkyl–transition metal bond, followed by ethylene insertion into an acyl transition metal bond.⁶

In all, it occurred to us that the general ability of transition metals to promote polymerization seems to be the reverse of their inclination to form stable π -alkene–metals. This pattern inspired us to a naive idea. Maybe it is possible to change the character of an essentially non-polymerizing transition metal such as palladium *by arranging a weak interaction between the metal and the alkene*

and in this way favor polymerization. Accordingly, we designed candidate complexes **3** (Scheme 1) with the following reasoning. (a) According to our experience cationic Pd(II) complexes coordinate alkenes more weakly than their neutral counterparts (*vide infra*). (b) We have proposed that bidentate, inflexible ligands, such as phenanthrolines, suppress β -hydrogen elimination by inducing a 'geometrical rigidity around the transition metal center'.⁷

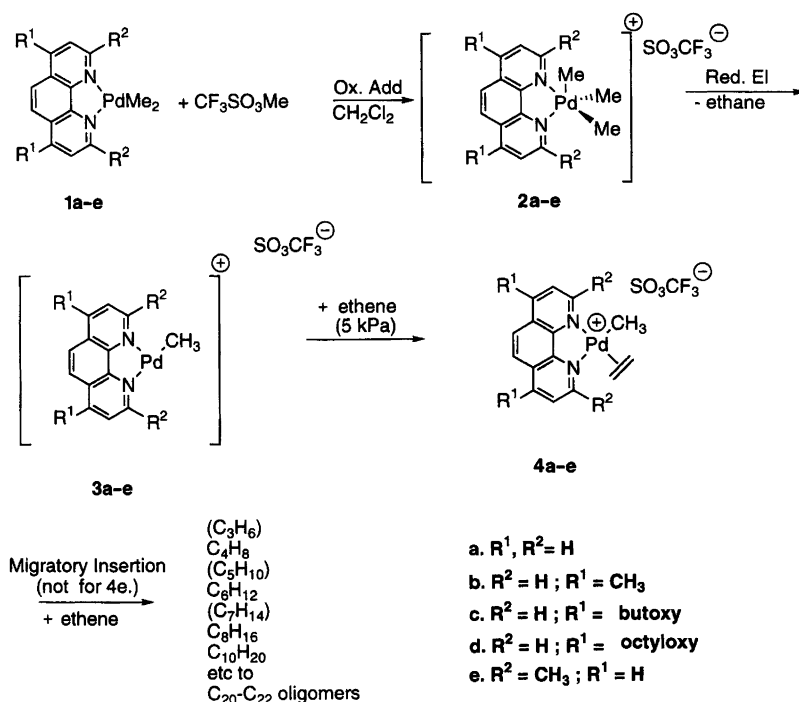
Success of this approach would be important for two reasons: (i) a general property of polymerization catalysts would be recognized and could be evaluated in more detail and (ii) with such knowledge at hand, rational design and tuning of catalysts should be feasible.

Results

The unsaturated complexes **3** appeared to be unstable, unless additional ligands such as acetonitrile or alkenes were present. These catalysts therefore had to be generated *in situ* from complexes **1**, which were prepared according to a literature procedure describing the preparation of **1a**.⁸ When complexes **3a–d** were generated in the presence of ethylene (5 atm) not only did fast dimerization take place, but also significant formation of hexenes and longer alkenes up to C_{20} . A series of control experiments proved that **3a–d** are prerequisites for oligomerization.

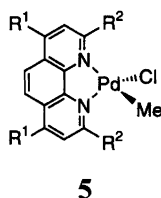
The choice of solvent is important, dichloromethane being the most superior. In ether and THF only butenes are formed, in acetonitrile even the dimerization is

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Scheme 1.

blocked. Chloroform is incompatible with **1** which rapidly reacts to give **5** even below 0°C .

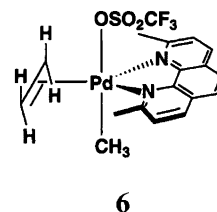


The different fractions of higher alkenes are mixtures both with respect to double bond position and branching. At an ethylene pressure of 5 kPa and room temperature (20°C) oligomers were formed with a turnover of 80 cycles per hour. In a typical run[†] (5 h), we obtained (GC) 80% butenes, 16.1% hexenes, 2.0% octenes and 0.8% decenes. Even higher olefins were detected. In order to determine the degree of branching the octene mixture formed by **3a** was hydrogenated. The predominant C_8 compounds were 3-methylheptane (39%) and *n*-octane (38%). If 1-decene was added to the reaction mixture, at 20°C and allowed to react for 5 h, considerable double bond isomerization as well as co-oligomerization was observed. Propene can also be oligomerized and in a preliminary study a slow formation of trimers could be seen.

When the reaction was performed in an NMR tube, no interaction between ethylene and **1** could be detected. Addition of methyl triflate ($\text{CF}_3\text{SO}_3\text{CH}_3$) resulted in the im-

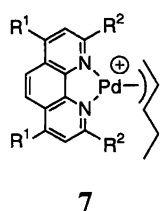
mediate formation of ethane (δ 0.86), most likely via fast reductive elimination from the transient species **2**. Although this compound eluded detection at -50°C , there exists ample literature precedence for similar types of palladium(IV) intermediate with the more coordinating iodide as the counter-ion. It seems reasonable that a coordinatively unsaturated cationic palladium(IV) species such as **2** should be more prone to reductive elimination than the corresponding neutral compound, where iodide coordinates.⁹ The addition of methyl triflate also caused instant line-broadening of the ethylene signal, indicating exchange between free and coordinated ethylene.

In contrast with **3a-d**, the neocuprine (2,9-dimethylphenanthroline) complex **3e** did not promote oligomerization. In the ^1H NMR spectrum, signals of coordinated ethylene appeared at δ 4.24 and 3.46 ppm. We suggest that a complex such as **6** is formed in accordance with the corresponding pentacoordinate neocuprine palladium.¹⁰



Dienes did not oligomerize as shown by butadiene which gave the $\eta^3(1,2,3)$ -pentadienyl complex **7** in 75% yield.

[†] The reaction is extremely sensitive to water.



In the case of **3e** no η^3 -allyl product was detected. Any reliable tendencies in the ethylene oligomerization activity for the complexes **3a-d** could not be discerned.

Discussion

The mechanism. It is easy to assume an ordinary coordination-type mechanism. A σ -alkyltransition metal associates with an alkene and a subsequent migratory insertion establishes the carbon-carbon bond-forming step. Repetition of these steps builds the chain. Competing β -hydrogen elimination interrupts the chain growth and the hydride formed may start up a new oligomerization sequence. However, different mechanisms have to be considered, especially as palladium is known to promote polymerizations by way of a mechanism involving carbocations.^{3,11} In our case such a route seems unlikely, since propylene is less prone than ethylene to oligomerize.¹² Besides, Sen has reported that donating ligands on palladium prevents carbocationic oligomerization.³ As expected carbocationic polymerization of dienes, unconjugated as well as conjugated, proceeds well.¹³ We obtain π -allyl complexes. Also a radical path appears improbable. Our reaction can readily be monitored by NMR spectroscopy and radicals would obscure NMR observations. Additionally, a radical polymerization of ethylene demands harsh reaction conditions.

Several observations are in accordance with a coordination mechanism. (I) In the presence of **3a-d** ethylene shows an exchange process in the ¹H NMR spectrum, indicating the formation **4a-d**. (II) When **3e** is exposed to ethylene coordination is observed. (III) Butadiene and **3a** form a π -allyl compound **7**, the expected primary product from a migratory insertion.

Factors favoring polymerization. We propose that weak interaction between metal and alkene is important for a polymerization catalyst. To relate such a suggestion to our results we discuss the factors commonly considered to be of importance for oligo- or poly-merization. The following factors are briefly discussed: high unsaturation of the transition metal, cationic catalysts, ligand-induced geometrical rigidity around the metal, weak interaction between metal and alkene.

Unsaturation of the transition metal. Commonly the number of electrons during the migratory insertion step is reduced from 16 to 14 for well defined catalysts to the left

of the periodic table, and this observation is interpreted in terms of high unsaturation of the metal being beneficial for polymerization.¹⁴ The Keim-type Ni(II) catalysts for oligomerization of ethylene are similar in this respect.¹⁵ Nevertheless, there exist significant exceptions, i.e. Brookhart's cationic η^5 -cyclopentadienyl(phosphine)- σ -alkyl-(π -ethylene)cobalt(III) catalysts are 18-electron compounds.¹⁶

Cationic catalysts. In the case of the Ziegler-Natta polymerization a consensus seems to have been established: an important role of the cocatalyst, like triethylaluminum, MAO (methyl aluminoxane), boron type Lewis acids, is to abstract a ligand of formal negative charge (mostly a chloride), thereby rendering the reaction center cationic.¹⁷ This idea has gained extensive support from the development of well defined unicomponent Ti(IV) and Zr(IV) cationic catalysts.^{14b-f, 18} Furthermore, it seems more than sheer coincidence that other well-defined catalysts are cationic as well.^{4, 16}

However, positive charge is not imperative. Accordingly, counter-ion participation in the insertion has been advocated.¹⁹

Neutral catalysts from the scandium triad are active.²⁰ The Keim type nickel(II) phosphonoacetates are also neutral.¹⁵ In the case of the commercially important and versatile chromium catalysts there exists no halide to abstract.²¹

Nevertheless, it is reasonable to claim that an essential role of the catalyst metal is to act as an electrophile. As the metal drains electron density from the coordinated alkene an electrostatic attraction between a partially positively charged alkene carbon and the partially negatively charged α -carbon of the alkyl chain [Fig. 1(a)] will appear. But is this the *sole* function of the metal, i.e., under appropriate reaction conditions can polymerization be performed by any cationic or strongly electrophilic, coordinatively unsaturated σ -alkyl transition metal? For the following reasons we suggest the answer to be no. (I) It is reasonable to assume that too much electrophilic character at the metal may induce a kinetically unfavorable situation, where repulsive, partially positive charge has been generated at the α -carbon of the alkyl chain [cf. Fig. 1(b)]. Accordingly, positive charge alone may not be a sufficient requirement for a transition metal to act as a catalyst.

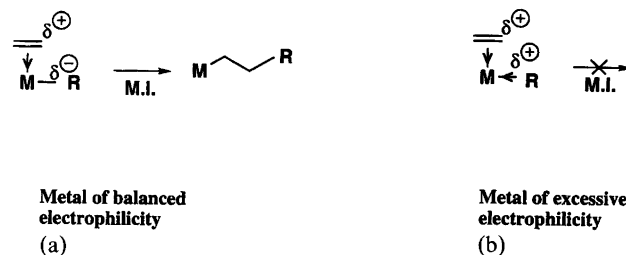


Fig. 1.

(II) Furthermore, the phenomenon that the metal can act as a Lewis acid withdrawing electron density from a coordinated alkene, rendering the alkene susceptible to nucleophilic attack, is extensively investigated and often successfully explored for synthetic purposes.²² Some of these π -alkene complexes are well characterized but more importantly, no oligo- or poly-merization has been reported in connection with studies on nucleophilic attack on coordinated alkene. Even though, in most of the cases the reaction conditions are disadvantageous for polymerization, it is more than likely that polymerization would have been accidentally discovered had polymerizing qualities been an inherent property of the electrophilic metal.

Geometrical rigidity around the transition metal center. We have previously proposed that geometrical rigidity around a transition metal should be generally considered a significant factor preventing β -hydrogen elimination.⁷ As chain growth is often interrupted by β -hydrogen elimination,^{20c, 23} geometrical rigidity around the catalyst metal should be favorable. In fact, this situation is frequently observed. For heterogeneous catalysts the metal is attached to a solid support of silica or magnesium chloride. Homogeneous catalysts acquire geometrical rigidity by ligands such as cyclopentadienyl, pentamethylcyclopentadienyl, indenyl or phosphonoacetates. It is interesting to note that if the phosphonoacetate is exchanged for more flexible 3-phosphonopropionate, oligomers are not observed.²⁴ We interpret such facts as support of our idea. At present, we are not aware of any polymerization catalyst devoid of ligands enforcing geometrical rigidity. Consequently, we find this factor a quite general one. Just recently, in connection with a study of intermediates in the successive insertion of carbon monoxide and alkenes, it was stated that 'apparently, the rigidity of the bidentate nitrogen ligand plays an important role by shutting off competing processes'.²⁵

Weak interaction between metal and alkene. A carbon-carbon σ -bond is around 20–25 kcal mol⁻¹ stronger than a carbon-carbon π -bond. This circumstance guarantees exothermicity in the migratory insertion step as long as the metal-alkene interaction is less than this difference and the rest of the ground state energetics are unchanged.

Calculations appear to be inconclusive in the matter of coordination bonding between alkene and metal. Some reports imply this interaction to be strong,²⁶ other reports suggest it to be weak.²⁷

For the following reasons we suggest *weak* interaction to be advantageous to oligomerization: (I) Isolated π -alkene-transition metals do not polymerize.²⁸ (II) In the periodic table the tendency strongly to bind alkenes is the reverse of that towards polymerization. (III) Polymerization catalysts are extremely poison sensitive. In accordance, highly desirable systems capable of copolymerizing functionalized alkenes are yet to be devised. (IV) As the coordination is at least partly lost in the transition state of the migratory insertion, this step is likely to proceed faster for a weakly coordinated alkene (denoted II in Fig. 2(a)) compared with a more strongly coordinated alkene [denoted I in Fig. 2(a)]. Of course, it may be objected that it may actually be the loss of metal-carbon σ -bond interaction that is crucial to the transition state.

However, this is less likely as the σ -bond will be present before as well as after the transition, whereas the π -interaction is lost. Furthermore, we observe fast polymerization of alkenes among early transition metals, although σ -carbon-metal bond strength increases towards the left-hand side of the periodic table.²⁹ This also suggests that the σ -carbon-palladium bond strength is of minor importance.

We further emphasize that as long as termination, as in the actual case, is constituted by β -hydrogen elimination it is crucial to suppress this reaction. Also in this case it should be advantageous with a weaker π -alkene interaction, since this is connected to a higher barrier towards elimination as depicted in Fig. (2b), as long as the kinetics parallel the thermodynamics.

In all, we interpret our results as consistent support for our leading hypothesis; weak coordination between the transition metal and the alkene is of importance for oligo- and poly-merization. Such a conclusion focuses upon a question: is there more than our personal experience, to support that cationic (π -alkene) palladium complexes are less stable than neutral? Kurosawa shows that the lability of cationic (π -alkene) palladium can be overcome by adopting the cyclopentadienyl group as an ancillary ligand. In part, he ascribes this stabilizing effect to the donating property of this ligand.³⁰ In our low-temperature NMR

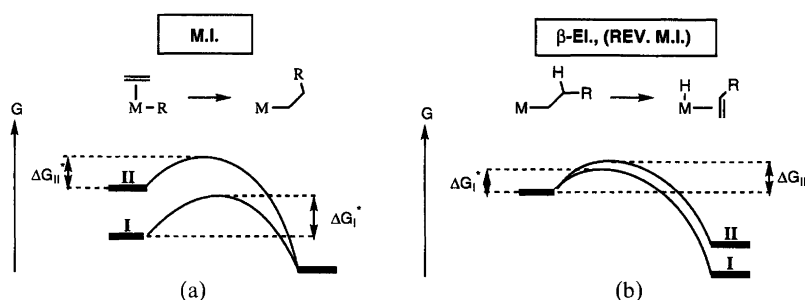


Fig. 2.

experiments we noticed fast exchange between coordinated and free ethylene. However, lability relates to kinetics and is not *a priori*, a result of a weak coordination. Nevertheless, in our case the assumption of weak interaction seems to be justified as rather weakly coordinating solvents interrupt any oligomerization beyond dimers. Furthermore, Sen explains that the less strong bonding to cationic palladium is due to weaker back-bonding.³¹ The same explanation is advocated for alkenes coordinating more weakly to Cr(III) compared with Cr(II).²¹

Conclusions

It is the intention of this report to advocate that *weak interaction* between the coordinated alkene and the transition metal is an important factor in the transition-metal oligo- and poly-merization of simple olefins.

Experimental

All glassware was washed with HNO₃ and dried in an oven (140 °C) overnight. Solvents were used as delivered or dried according to standard procedures.³² ¹H NMR chemical shifts are reported in ppm relative to solvent resonance: CDCl₃ δ 7.24; CD₂Cl₂ δ 5.31. Elemental analyses were provided by *Analytische Laboratorien*, Gummersbach. All reactions were performed under an argon atmosphere. Ethylene for oligomerization was dried by passage through CaSO₄.

4,7-Dibutoxy-1,10-phenanthroline. 4,7-Dihydroxy-1,10-phenanthroline (2.12 g, 10.0 mmol) was placed in a 100 ml flask equipped with a condenser and dissolved in 75 ml of *N,N*-dimethylformamide. NaH (0.90 g, 80% with oil, 30 mmol) was added, the slurry was stirred for 30 min at 25 °C before addition of freshly distilled 1-bromobutane (6.85 g, 50 mmol). The temperature was raised to 60 °C for 3 h. The cooled reaction mixture was poured into 100 ml of H₂O, extracted with 3 × 80 ml of CH₂Cl₂. The combined organic phases were dried with MgSO₄, concentrated *in vacuo* and recrystallized (CH₂Cl₂-diethyl ether) to yield 2.13 g (67%) of pure 4,7-dibutoxy-1,10-phenanthroline as a light colored solid. ¹H-NMR (250 MHz, CD₃Cl): δ 8.97 (d, *J* = 5.3 Hz, 2 H) 8.16 (s, 2 H) 6.96 (d, *J* = 5.3 Hz, 2 H) 6.96 (d, *J* = 5.3 Hz, 2 H) 4.25 (t, *J* = 7.5 Hz, 4 H) 1.97 (m, 4 H) 1.65 (m, 4 H) 1.06 (t, *J* = 7.3 Hz, 6 H); ¹³C NMR (100 MHz, CH₃Cl): δ 207.0, 163.3, 150.5, 121.3, 119.5, 104.0, 69.4, 30.9, 19.3, 13.9.

4,7-Dioctyloxy-1,10-phenanthroline. See the procedure for 4,7-dibutoxy-1,10-phenanthroline but exchange 1-bromobutane for 1-bromooctane. Yield 71%. ¹H NMR (250 MHz, CD₃Cl): δ 8.97 (d, *J* = 5.3 Hz, 2 H) 8.19 (s, 2 H) 6.96 (d, *J* = 5.3 Hz, 2 H) 4.24 (t, *J* = 6.4 Hz, 4 H) 1.7–1.1 (m, 20 H) 0.90 (t, *J* = 6.9 Hz, 6 H)

Oligomerization of Ethylene. A Fisher–Porter tube (F–P tube) was cleaned with *aqua regia* and with soap and H₂O, dried in an oven at 140 °C overnight. The palladium complex **1a–f** (0.19 mmol) was placed in the F–P tube. CH₂Cl₂ (5 ml, Aldrich sure seal quality) was added giving a clear yellow solution. Ethylene pressure (5 atm) was applied, when the system was saturated, methyl triflate (0.19 mmol, 28 μl) was injected through a septum. The yellow color disappeared immediately. The F–P tube was constantly fed with 5 atm pressure of ethylene for 5 h. The amount of oligomers formed was analysed by GC[†] with an internal standard. The oligomers were identified by GC–MS.*

Methyl (2,9-dimethyl-1,10-phenanthroline)ethylenepalladium(II) trifluoromethanesulfonate (5). To a solution of dimethyl(2,9-dimethyl-1,10-phenanthroline)palladium (37.5 mg, 0.11 mmol) and butadiene (4 ml, 0.15 mmol) in dry CH₂Cl₂ at –10 °C under N₂, was added methyl trifluoromethanesulfonate (80 mg, 0.5 mmol). The solution was concentrated *in vacuo*. Yield: 30 mg, 54%. ¹H NMR (400 MHz, CD₂Cl₂): δ 8.33 (d, 2 H), 7.87 (s, 2 H), 7.75 (d, 2 H), 4.24 [app. d, 2 H, *J* = 14.4 Hz, HC = CH(olefinic)], 3.46 [app. d, 2 H, *J* = 14.1 Hz, HC = CH(olefinic)], 3.32 (s, 6 H, CH₃-phen), 0.27 (s, 3 H, CH₃-Pd).

1,10-Phenanthroline[*syn/anti*-(1,2,3-η)-pentyl]palladium tetrafluoromethanesulfonate (6). To a solution of butadiene (g, 25 ml, 1 mmol) and dimethyl(1,10-phenanthroline)palladium (94.0 mg, 0.30 mmol) in 20 ml of dry CH₂Cl₂ under Ar, was added methyl trifluoromethanesulfonate (0.28, 0.30 mmol) at –10 °C. After 0.5 h the solvent was evaporated off, the yellow precipitate was recrystallized (acetone–hexane) and dried *in vacuo*. Yield 0.11 g (0.22 mmol), 75%, *anti/syn* = 16/100. ¹H NMR (400 MHz, acetone-*d*₆) *syn*: δ 9.45 (d, 1 H), 9.15 (d, 1 H), 9.01 (d, *J* = 8.0 Hz, 2 H), 8.34 (s, 2 H), 8.20 (dd, 2 H), 6.06 (dt, *J* = 12.3, 7.0 Hz, 1 H), 4.61(d, *J* = 7.0 Hz, 1 H), 4.52 (ddd, *J* = 12.1, 8.0, 4.0, 1.0, 1 H), 3.76 (d, *J* = 12.3 Hz 1 H), 2.30–2.15 (m, 2 H), 1.33 (t, *J* = 7.5 Hz, 3 H). *anti*: δ 9.66 (d, *J* = 5.0 Hz, 1 H), 9.28 (d, *J* = 5 Hz, 1 H), 8.98 (d, *J* = 8.5 Hz, 1 H), 8.92 (d, *J* = 8.5 Hz), 8.53 (s, 2 H), 8.47 (dd, *J* = 8.5, 5.0 Hz, 1 H), 8.15 (dd, *J* = 8.5, 5.0 Hz, 1 H), 6.00 (dt, *J* = 13.5, 7.7 Hz, 1 H), 5.44 (app. q, *J* = 7.7 Hz 1 H), 4.62(d, *J* = 7.7 Hz, 1 H), 4.03 (d, *J* = 13.5 Hz, 1 H), 1.80 (m, *J* = 7.4 Hz, 2 H) 1.19 (t, *J* = 7.4 Hz, 3 H). ¹³C NMR (100 MHz, acetone-*d*₆): δ 155.4, 153.4, 152.4, 151.2, 149.7, 146.1, 145.3, 140.8, 131.0, 128.5, 127.3, 123.8, 120.1, 118.1, 114.5, 87.0, 85.1, 62.5, 59.2, 24.6, 23.9, 15.6, 14.1.

[†] 2 GC Varian model 3700 equipped with 15 m × 0.15 mm dimethylpolysiloxane capillary column.

* GC–MS: GC, Varian model 3400 equipped with 25 m × 0.15 mm DB-5. MS, Finnigan 4000 ms. Reference substance from Aldrich and Fluka.

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