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Catalytic Hydrogenolysis at Low Temperature and Pressure of Polyethylene and Polypropylene to Diesels or Lower Alkanes by a Zirconium Hydride Supported on Silica-Alumina: A Step Toward Polyolefin Degradation by the Microscopic Reverse of Ziegler–Natta Polymerization

Véronique Dufaud* and Jean-Marie Basset*

Transition metal catalyzed polymerization of ethylene and propylene was discovered in the 1950s by Ziegler and Natta.[1] Since then, there have been many applications and a large production of these polymers. However, at the end of this century, the presence of such polyolefins in our daily life has reached such a level that its environmental consequences can no longer be underestimated. The solutions to overcome this environmental challenge with catalytic methods at low temperature and pressure are not known at the moment.[2] The scientific reasons for this deficit may be divided in two categories: the chemical inertness of polyolefins and the thermodynamic limitations to achieving the reverse of the Ziegler–Natta polymerization.

Although they are formed from olefins, polyolefins such as polyethylene or polypropylene are not "olefinic" materials since they become "paraffinic" upon polymerization. These long-chain paraffinic materials are extremely inert, and there is no simple way to transform them selectively, especially at moderate temperature, into valuable products.

It would be very fascinating to transform polyolefins into olefinic oligomers or monomers, which is theoretically possible from a mechanistic point of view according to the principle of microreversibility. The insertion of an olefin into a metal–alkyl bond, the key step in the Ziegler–Natta polymerization,[3] can be considered as the microscopic reverse of the β-alkyl transfer [Eq. (a); the polymer chain is represented by Ⓟ].[4] However, since such transformations are thermodynamically impossible at moderate temperature, it is necessary to find solutions to overcome this limitation.

(a)

We report here that it is possible to polymerize ethylene or propylene to the corresponding polyolefins with a zirconium hydride supported on silica-alumina.[5] We also demonstrate that under hydrogen the same catalyst that can polymerize ethylene or propylene is able to cleave statistically all the C–C bonds of polyethylene or polypropylene to a range of short-chain saturated oligomers, diesels, or eventually methane, ethane, and lower alkanes.

We recently disclosed a new catalyst that is able to carry out the catalytic cleavage of the C–C bonds in several simple alkanes under hydrogen. The catalyst is a well-defined silica-supported zirconium monohydride ($(\equiv SiO)_3ZrH$ (**1**))[6–8] that is obtained by surface organometallic chemical reactions.[9] For example, **1**, which is very electrophilic,[10] is able to cleave the C–C bonds of propane, butanes, and pentanes (but not ethane) under a moderate hydrogen pressure (< 1 atm) and at mild temperatures (typically 25–150 °C).[11, 12] Considering that polyolefins are simply long-chain hydrocarbons, the catalytic cleavage of the C–C bonds in these higher alkanes might be possible with our electrophilic silica-supported zirconium hydride or some more strongly electrophilic supported zirconium hydride.

To render the supported zirconium hydride even more electrophilic than on silica, we treated tetraneopentylzirconium with the surface silanol groups of a silica-alumina that was partially dehydroxylated at 500 °C (silica-alumina$_{500}$). The reaction led to the formation of a surface species which can be formulated as $(\equiv SiO)ZrNp_3$ (**2**). Treatment of **2** with hydrogen at 150 °C provided the formation of a zirconium hydride supported on silica-alumina with the concommitant generation of silicon dihydride and aluminium hydride. Based on what is known for the structure of **1** on pure silica, we propose two structures for the zirconium hydride supported on silica-alumina (Scheme 1): One can be formulated as $(\equiv SiO)_3ZrH$ (**3a**), in which the zirconium hydride is a monohydride grafted to silica-alumina through three covalent bonds. This was already demonstrated for pure silica by several techniques including EXAFS.[8] The second structure **3b** is very similar. However, aluminium hydride groups could be in close proximity to the zirconium center, and the zirconium atom would be even more electrophilic than on pure silica.

When **3** was exposed to an ethylene pressure of 200 torr at room temperature, the IR spectrum of the solid showed the

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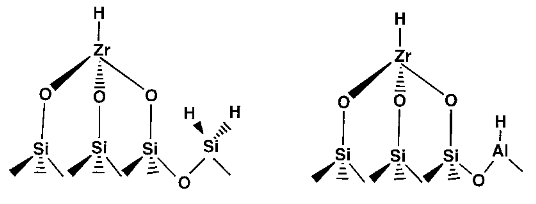


3a **3b**

Scheme 1. Proposed structures for **3**.

immediate disappearence of the band at 1635 cm^{-1} for the ν(Zr–H) vibration (Figure 1a and b). Simultaneously, very intense bands appeared in the region of 2970–2850 cm^{-1} and at 1380 cm^{-1}, which is characteristic of polyethylene.[13] The same catalyst is able to polymerize propylene at room temperature to polypropylene, as evidenced by IR spectroscopy (intensive, characteristic bands associated for ν(C–H) and δ(C–H) vibrations of polypropylene were observed).[13]

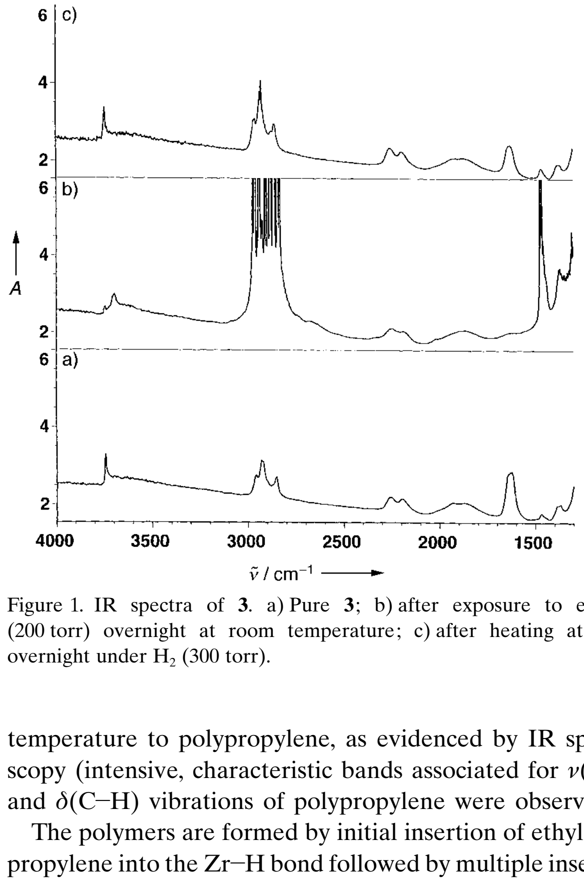


Figure 1. IR spectra of **3**. a) Pure **3**; b) after exposure to ethylene (200 torr) overnight at room temperature; c) after heating at 150 °C overnight under H_2 (300 torr).

The polymers are formed by initial insertion of ethylene or propylene into the Zr–H bond followed by multiple insertions of the monomer into the resulting Zr–alkyl bond.[14] When the polyethylene bound to zirconium supported on silica-alumina was heated to 150 °C overnight under hydrogen (300 torr), hydrogenolysis of the polymer occured, as demonstrated by IR spectroscopy, gas chromatography/mass spectroscopy, and other experiments. The very intense bands in the IR spectrum at 2970–2850 cm^{-1} and 1380 cm^{-1} (attributed to the ν(C–H) and δ(C–H) vibrations of polyethylene, respectively) decreased dramatically in intensity with time, whereas the band for the ν(Zr–H) vibration at 1635 cm^{-1} reappeared (Figure 1c). Only methane, ethane, and higher alkanes were detected in the gas phase, which indicates that all the C–C bonds of the polymer were cleaved progressively under these conditions. After 15 hours of reaction only methane and ethane were detected. Similar results were obtained for polypropylene bound to zirconium supported on silica-alumina. Under appropriate conditions, catalyst **3** is apparently capable of catalyzing both olefin polymerization and hydrogenolytic degradation of the resulting polymer.

A logical application of this polymerization/hydrogenolysis reaction is therefore the degradation of commercial polyolefins under analogous conditions. In another series of experiments, samples of polyethylene of low molecular weight (C_{18} to C_{50}, Figure 2a) were brought into contact with catalyst **3** under hydrogen (1 atm) at 150 °C for varying periods of time. As represented on Figures 2 and 3, degradation of the polymer occurred; the product distribution depends on the reaction time.

After one hour of reaction 5 % of the starting polyethylene had been converted into light alkanes. The distribution of the oligomers underwent significant changes (Figure 2b): The proportion of lower oligomers increased (especially below C_{18}), which demonstrates catalytic cleavage of the C–C skeleton of the initial polyethylene. Furthermore, in the fraction from C_{18} to C_{50}, for which the starting polymer contains only oligomers with an even number of carbon atoms, new peaks with an odd number of carbon atoms were detected. This shows that there is a statistical cleavage of all C–C bonds in the polymeric chain by the zirconium hydride. After two hours of reaction 25 % of the starting polyethylene was converted into lower alkanes ($< C_9$, Figure 3). The amount of oligomers with an even number of carbon atoms was almost the same as that of oligomers with an odd number of carbon atoms; there was a broadening of the molecular-weight distribution and a shift toward the oligomers of low molecular weight (Figure 2c). After five hours of reaction only a fraction of oligomers between C_{10} and C_{17} persisted (corresponding to the hydrocarbons in diesel), and 84 % of the initial polyethylene was converted into lower alkanes (C_1 to C_9; Figure 3). When the reaction was carried out for 62 hours, all the starting polyethylene was converted into light alkanes (Figures 2e and 3). Therefore, the reaction time has an effect on the distribution of product oligomers and light alkanes. For alkanes with less than nine carbon atoms, one obtains predominantly pentanes and hexanes at low conversion, whereas methane and ethane are the predominant products at higher conversions. This was expected from previous studies on alkane hydrogenolysis with similar catalysts.[11] In conclusion, catalyst **3** is able to cleave polyethylene under a low hydrogen pressure and at very moderate temperature. Further experiments carried out with low-density polyethylene of higher molecular weight ($M = 125000$) provided essentially similar results: 100 % conversion of the initial polyethylene into saturated oligomers (after 5 h) or lower alkanes (last ten hours) at 150 °C. Catalyst **3** is also able to cleave commercial isotactic polypropylene ($M = 250000$) under hydrogen at about 190 °C and in the absence of any solvent. For example, 40 % of the starting polypropylene was converted into lower alkanes after 15 hours of reaction at 190 °C (see Experimental Section). Furthermore, the reaction could be carried out in the presence of a solvent which is not hydrogenolyzed under reaction conditions (e.g. decaline, owing to steric constrains on β-alkyl elimination).[15]

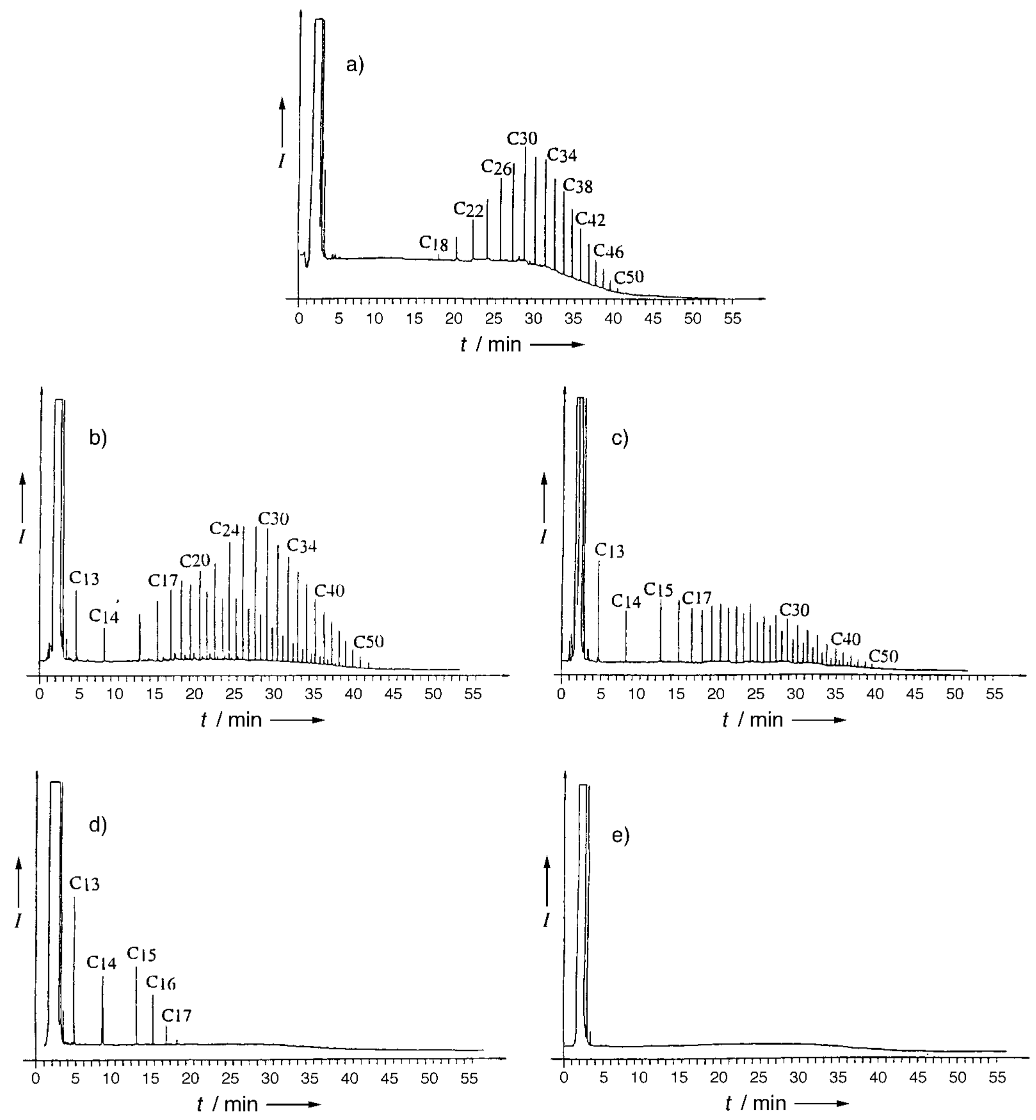


Figure 2. Gas chromatographic determination of the oligomer distribution. a) Initial polyethylene; b) after 1 h; c) after 2 h; d) after 5 h; e) after 62 h of reaction.

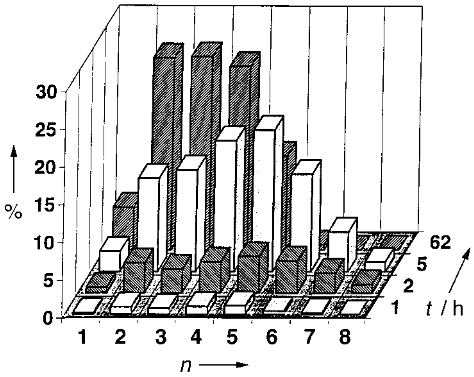
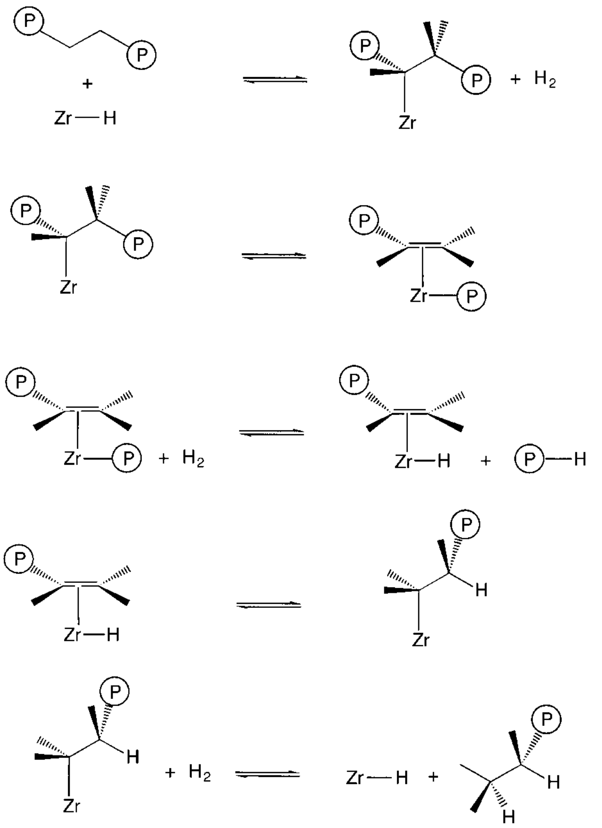


Figure 3. Product distribution of light alkanes C_nC_{2n+2} as a function of time *t*.

The mechanism of such polymerization/hydrogenolysis reactions is possibly based on elementary steps already known in organometallic chemistry, mainly the equilibrium insertion$\rightleftharpoons\beta$-alkyl transfer. In and of itself, the β-alkyl transfer (the microscopic reverse of olefin insertion) would be thermodynamically unfavorable. However, based on our observations, we propose that a subsequent hydrogenation of olefinic double bonds renders the process of "hydrogenolytic polymer degradation" exothermic (Scheme 2).

The first step (Scheme 2) is a facile, unselective activation of a C–H bond in the paraffinic chain, which occurs by σ-bond metathesis with liberation of hydrogen. This kind of activation is now well described for early transition metals with a d^0 configuration[16] as well as for silica-supported zirconium hydride.[8, 11] The polymer is then unselectively grafted to the zirconium center through a σ bond. This can be proven by the fact that, at low conversion and in all the cases we described, statistical cleavage of C–C bonds along the polymer backbone produced small amounts of methane or ethane. This indicates that the C–H bonds at the ends of the oligomers are not particularly favored over those in the rest of the chain. Once the polymeric chain is linked to the zirconium center, a β-alkyl transfer is observed (Scheme 2, second reaction); a fraction of



Scheme 2. Proposed mechanism for the hydrogenolytic degradation of polyethylene.

the polymeric chain is grafted through a sigma bond to the metal, and another fraction is π-bonded through its terminal double bond to the metal. The final steps (Scheme 2, last three reactions) involve removal of the polymers by cleavage of the zirconium–carbon bond and hydrogenation of the terminal double bond.

Experimental Section

The IR spectra were recorded on a Nicolet 550FT spectrometer, and the CP-MAS ^{13}C NMR spectra (75.47 MHz) on a Brucker MSL-300 spectrometer. The 90° ^{1}H pulse length was 5 μs, the contact time 15 ms, and the recycle delay 2 s. $ZrNp_4$ was prepared by a literature procedure.[17] All manipulations were performed in a glovebox or with high-vacuum techniques. Light alkanes were analyzed by gas chromatography (GC) with a capillary column of fused silica (CHROMPACK Al_2O_3/KCl; 50 m × 0.32 mm). Oligomers were extracted from the reaction medium with hot decaline and analyzed by gas chromatography (capillary column HT5 0.1 mm, 12 m, 0.22 mm internal diameter, covered with alumina). Typical chromatograms are given in Figure 2.

$(\equiv SiO)ZrNp_3$ (**2**): The reaction between $ZrNp_4$ and the surface silanol groups of a deuterated silica-alumina (Ketjen, 25% Al, 375 m^2g^{-1}, dehydroxylated at 500 °C) led to the generation of a zirconium alkyl species on the surface and the liberation of about 1 mol of $[D_1]$2,2-dimethylpropane per mole of grafted zirconium [Eq. (b)]. The surface

$$\equiv Si{-}OH(D) + ZrNp_4 \rightarrow (\equiv SiO)ZrNp_3 + NpH(D) \qquad \text{(b)}$$

species was characterized with analytical and spectroscopic techniques, and the structure $(\equiv SiO)ZrNp_3$ (**2**) was proposed, in which the zirconium atom is σ-coordinated by three neopentyl ligands and grafted to the surface through one covalent bond to oxygen. **2**: Elemental analysis: C:Zr = 14:1 (expected value: 15:1); IR: $\tilde{\nu} = 2949$ ($\nu_{as}(CH_3)$), 2900 ($\nu_{as}(CH_2)$), 2865 ($\nu_s(CH_3)$), 2822 ($\nu_s(CH_2)$), 1467 ($\delta_{as}(CH_3)\delta_s(CH_2)$), 1362 cm^{-1} ($\delta_s(CH_3)$); CP-MAS ^{13}C NMR: $\delta = 33.1$ ($CH_2C(CH_3)_3$), 94.5 ($CH_2C(CH_3)_3$). Deuterolysis of **2** gave 2.7 mol of $[D_1]$2,2-dimethylpropane (expected value: 3 mol). Deuterolysis of **2** after polymerization gave 2.16 mol of $[D_1]$2,2-dimethylpropane (expected value if all the zirconium atoms are propagating centers: 2 mol).

$(\equiv SiO)_3ZrH$: Treatment of **2** with H_2 at 150 °C led to the formation of a zirconium monohydride supported of silica-alumina along with the concommitant generation of silicon dihydride and the partial formation of an aluminium hydride [Eq. (c)]. The reaction was monitored by IR

$$(\equiv SiO)ZrNp_3 + \equiv SiOSi\equiv + \equiv SiOAl{=}$$
$$\xrightarrow{H_2} (\equiv SiO)_3ZrH + \equiv SiH_2 + {=}AlH + C_nH_{2n+2} \qquad \text{(c)}$$

spectroscopy. The broad band at 1635 cm^{-1} for the ν(Zr–H) vibration was displaced under D_2 and quantitavely restored under H_2. The band for the ν(Al–H) vibration was observed as a very weak signal at 1933 cm^{-1}. The bands for $\nu(Si(H)_2)$ vibrations appeared at 2260 and 2189 cm^{-1}.[8]

Polymerization of ethylene and propylene and hydrogenolytic depolymerization of the resulting polymers: These reactions were followed by IR spectroscopy. The monomer (ethylene or propylene, 200 torr) was introduced into the infrared cell and allowed to react with **3** at room temperature for 2 h. The excess of monomer was then removed for 4 h under vacuum. The polymer bound to zirconium supported on silica-alumina was then heated at 150 °C overnight under H_2 (300 torr).

Hydrogenolysis of polyethylene: A polyethylene of low molecular weight with a broad range of molecular weight (C_{20} to C_{50}; only oligomers with an even number of carbon atoms are included, see Figure 2a) was used for the kinetic experiments. In a typical experiment **3** (70 mg, 3 wt% Zr, 0.023 mmol Zr) was placed in a glass reactor with a volume of 482 mL, and polyethylene (115 mg; corresponding to 8 mmol of CH_2 units) was then introduced under an inert atmosphere. A hydrogen pressure of 10^5 Pa (corresponding to 19.7 mmol of H_2) was established in the reactor at room temperature. The reactor was heated at 150 °C for several hours. The hydrogenolyses were also conducted with a low-density polyethylene ($M = 125000$) from Aldrich. The conversion into lower alkanes (C_1 to C_9) was calculated by dividing the number of moles of carbon in the product mixture by the number of moles of starting polymer (obtained by dividing the mass of the polymer by 14). The yields of the individual products (C_n) was determined by dividing the number of moles of carbon for a given product by the total number of moles of carbon in the starting polymer.

Hydrogenolysis of polypropylene: The polypropylene ($M = 250000$) used in these experiments was purchased from Aldrich. According to the procedure described above, 40% of the starting polypropylene was converted into lower alkanes (methane: 11.6, ethane: 5.7, propane: 6.2, butanes: 7.2, pentanes: 6, hexanes: 2.8, heptanes: 0.5%) after 15 h at 190 °C.

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A Spin-Frustrated System Composed of Organic Radicals and Magnetic Metal Ions

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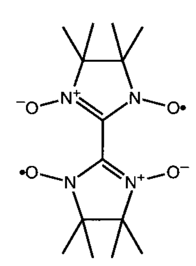
Antiferromagnetically coupled spins in polynuclear complexes of paramagnetic metal ions[1] and π-cross-conjugated organic polyradicals[2] can be arranged in triangular, "butterfly"-shaped, tetrahedral, or cubane-like structures and combinations of these topologies. Consequently, these materials provide ample opportunities for delineating competing interactions in which two neighboring spins have to align in parallel in spite of the antiferromagnetic coupling. When a degenerate ground state ensues, the system is referred to as spin-frustrated. The versatility of molecule-based magnetic materials will be much enhanced in heterospin systems consisting of paramagnetic metal ions in conjunction with organic free radical bridging ligands.[3] The diradical 2,2′-bis(1-oxyl-3-oxide-4,4,5,5-tetramethylimidazolinyl) (bnn), which was first reported by Ullman et al.[4] and later characterized by Rey et al. with respect to its magnetic properties,[5] captured our attention as an interesting bis-bidentate paramagnetic ligand for magnetic metal ions. We report here a new spin-frustrated system consisting of manganese(II) bis(hexafluoroacetylacetonate) ($[Mn(hfac)_2]$) and bnn with a butterfly spin arrangement.



bnn

Complexation was effected by mixing anhydrous $[Mn(hfac)_2]$ and bnn. Dark green crystals were obtained, and their composition was found to be 2:1, $[\{Mn(hfac)_2\}_2(bnn)]$, by elemental analysis.[6] The crystal and molecular structure (Figure 1) was determined by X-ray crystallographic analysis.[7] The molecular structure of bnn in the complex is very similar to that reported for free bnn.[5] The C1–C8 bond length of 1.44(2) Å is almost the same as that in the free ligand (1.439(3) Å), and the dihedral angle between the two "Ullman's nitronyl nitroxide radical" moieties is 55° in the complex as well as in bnn itself. These similarities suggest that the bnn ligand forms the $[Mn(hfac)_2]$ complex with minimal structural perturbation and that the magnetic interaction between the two radical centers should only be marginally modified by complexation.

Magnetic measurements of $[\{Mn(hfac)_2\}_2(bnn)]$ were performed on a SQUID susceptometer/magnetometer. The

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