The mechanism of this reaction and the exact nature of the copper species involved in this highly efficient catalytic process still need to be established. Nevertheless, this unprecedented regiodivergent catalytic parallel kinetic resolution with an organometallic reagent supports the notion that the oxidative addition might be a very fast process and reductive elimination is instead a regio- and stereodetermining step.

Experimental Section

General procedure: A solution of [Cu(OTf)$_2$] (10.83 mg, 0.030 mmol) and **1** (32.3 mg, 0.06 mmol) in anhydrous toluene (4.0 mL) was stirred at room temperature for 40 min. The colorless solution was cooled to $-78\,^{\circ}C$, and subsequently solutions of racemic vinylepoxide (2.0 mmol) in toluene (1.0 mL) and R_2Zn (3.0 mmol) in toluene were added. The resulting light yellow solution was quenched with saturated aqueous NH_4Cl (5.0 mL) once the reaction reached completion (GC analysis). Extraction with Et_2O and evaporation of the dried ($MgSO_4$) organic phase gave the crude product, which was subjected to flash chromatography (see Supporting Information). Enantioselectivities were determined by chiral GC (CP-cyclodex-β-column).

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From Oligomers to Conducting Polymers of the Metal–Dinitrogen Functionality[**]

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This report opens, in the use of dinitrogen, a completely new avenue, which is derived neither from any of the bioinspired processes[1] nor from the objectives pursued so far in the metal-assisted dinitrogen chemistry.[2, 3]

Although $\mathrm{:N{\equiv}N:}$ and $[\mathrm{:C{\equiv}C:}]^{2-}$, the deprotonated form of acetylene, are isoelectronic, this similarity has not helped in establishing a practical parallelism between the two species, namely in the triple bond cleavage[2h–j] or in their use in material science. In the latter context, the polymeric forms of acetylene, such as polyacetylene and related cumulenes, have a relevant importance.[4, 5] This report deals with the oligomerization of the metalla–dinitrogen functionality and with a perspective to polymerize this moiety. This entry into material science using dinitrogen opens a new avenue in this domain. We report herein how we were able to achieve the unprecedented oligomerization of the metalla–dinitrogen functionality and thereby anticipating and planning the formation of the corresponding polymers.

The alkylation of [WCl_4(dme)] (DME = dimethoxyethane) using MesMgBr (Mes = 2,4,6-$(CH_3)_3C_6H_2$) under a nitrogen atmosphere occurs with a fast absorption of dinitrogen

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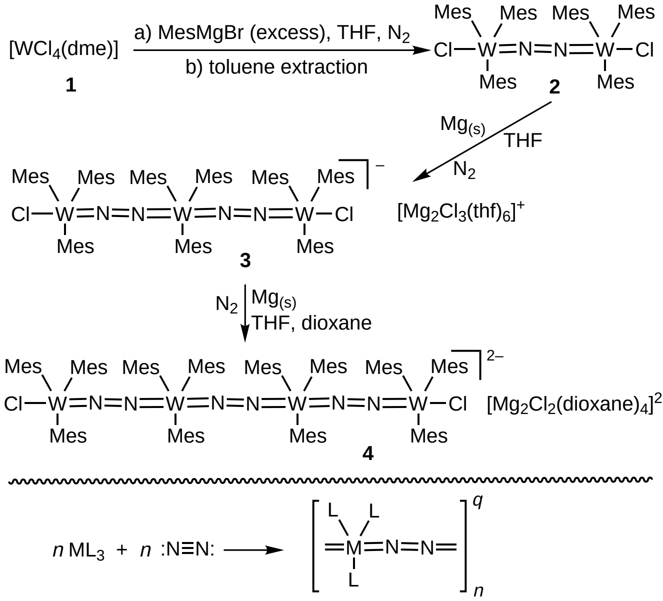
leading to the intermediate formation of a red solid, which was then extracted with toluene, thus producing **2** as a diamagnetic, green crystalline material (Scheme 1). Complex



Scheme 1. Preparation of compounds **2**–**4**.

2 was fully characterized both in solution and in the solid state (W−N 1.846(8), N−N 1.180(16) Å; W-N-N = 180.0°). Complex **2** undergoes a stepwise reduction under N_2 atmosphere leading to **3**[6] and then to **4** (Scheme 1), as controlled by the W/Mg stoichiometric ratio. The occurrence of the reaction can be followed by the expected absorption of N_2 and a change in the color of the solution from green (**2**) to red (**3**) and then to violet (**4**). Both **3** and **4** are diamagnetic, so that the conversion of a dinuclear→trinuclear→tetranuclear dinitrogen compound can be followed by ^{1}H NMR. The most relevant structural parameters of **3** are represented by the bond length sequence W−N 1.787(7), N−N 1.272(10), N−W 1.881(7), W−N 1.861(7), N−N 1.273(11), and N−W 1.801(7) Å, while those of **4** are in the caption of Figure 1.[7] Although there are significant differences in the W−N and N−N bond distances for **2**, **3**, and **4** depending on the oligomerization degree, these structural parameters are in reasonable agreement with the proposed cumulene structure.[2f–i, 8, 9] The tungsten–dinitrogen oligomers can be seen as chains with two perpendicular π-systems made of alternating metal and two nitrogen atoms and carrying two electrons for each nitrogen atom and the d electrons of tungsten. Each one of these systems therefore resembles the π-system of an organic polyene, with as many carbon atoms as the total number of tungsten and nitrogen atoms in the considered oligomer. The calculations performed on the dinuclear, trinuclear, and tetranuclear species show a stable singlet state with a large HOMO–LUMO gap.

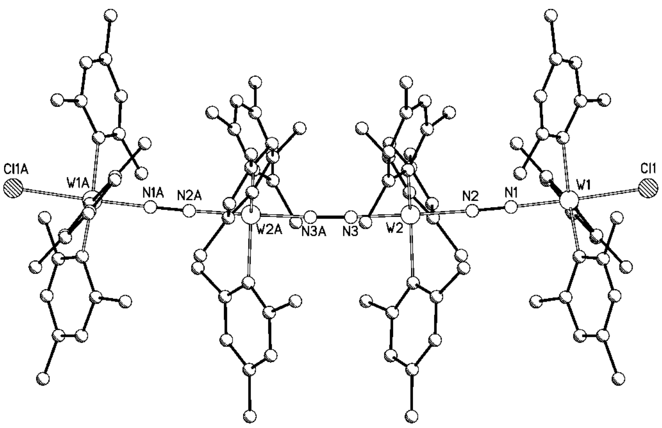


Figure 1. Ball-and-stick diagram for the anion in complex **4**. Selected bond lengths [Å] and angles [°]: W1-Cl1 2.494(2), W1-N1 1.825(8), W1-C_{av} 2.145(10), N1-N2 1.212(12), W2-N2 1.931(7), W2-N3 1.855(8), W2-C_{av} 2.166(9), N3-N3A 1.264(15); Cl1-W1-N1 177.9(2), W1-N1-N2 178.8(7), N1-N2-W2 177.9(7), N2-W2-N3 178.8(3), W2-N3-N3A 177.4(4). The notation A indicates the symmetry transformation $-x+1, y, -z+\frac{1}{2}$.

The sequence displayed in Scheme 1 anticipates the existence and the electronic structure of hypothetical metalla–dinitrogen polymers, for which a strong theoretical support is presented here. We have used the extended-Hückel method in the tight-binding scheme[10] to study the electronic structure of the $[-(\mathrm{H})_3\mathrm{W}{-}\mathrm{N}_2{-}]_n^q$ hypothetical polymers, **5**, with different electron counts obtained by varying the charge of the $[(\mathrm{H})_3\mathrm{W}]$ metal fragment.[11] In particular, we considered d^2, d^3, or d^4 metal configurations corresponding to $[-(\mathrm{H})_3\mathrm{W}{-}\mathrm{N}_2{-}]_n^{n+}$, $[-(\mathrm{H})_3\mathrm{W}{-}\mathrm{N}_2{-}]_n$, and $[-(\mathrm{H})_3\mathrm{W}{-}\mathrm{N}_2{-}]_n^{n-}$ polymers. The energy levels for the planar WL_3 fragment show the usual pattern expected for a D_{3h} symmetry. At the lowest energies, there is an e set, of predominantly metal d_{xz} and d_{yz} character, a slightly higher $a_1(d_{z^2})$, and then a second e set of predominantly metal d_{xy} and $d_{x^2-y^2}$ character, much higher in energy. The band structure of the considered polymer is shown in Figure 2a, where only the highest occupied and lowest unoccupied crystal orbitals are reported and the Fermi level is referred to a d^2 configuration. The projection of the d metal and carbon p_x and p_y orbitals (the z-axis is assumed to be parallel to the axis of the polymers) of the density of states (DOS) for **5**, Figures 2b and 2c, clarify the nature of these bands. The main feature of the band structure is the presence

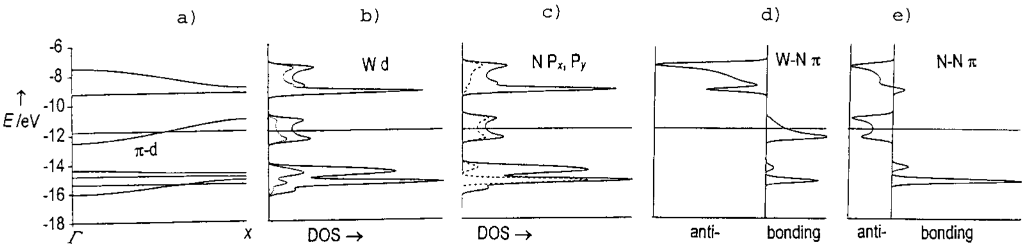


Figure 2. a) Band structures of the $[-(\mathrm{H})_3\mathrm{W}{-}\mathrm{N}_2{-}]_n^q$ polymer. b, c) Density of states (solid lines) with the projection of the b) metal d orbitals and c) N p_x and p_y orbitals (dashed lines). d, e) Crystal-orbital overlap population (COOP) curves for d) N−N and e) W−N π-bonding. The horizontal lines indicate the Fermi energy for the $[-(\mathrm{H})_3\mathrm{W}{-}\mathrm{N}_2{-}]_n^{n+}$ polymer with d^2 metal configuration.

of an occupied, high lying, dispersed band arising from the interaction of the e (d_{xz}, d_{yz}) set and the π* orbitals of the dinitrogen unit (hereafter called π-d band) with W–N bonding and N–N antibonding character, as shown by the crystal-orbital overlap population (COOP) curves, Figures 2d and 2e. The next lowest occupied crystal orbitals have a high contribution from the occupied σ- and π-orbitals of the N_2 moiety, while the lowest unoccupied crystal orbital is a flat band of essentially metal e (d_{xy}, $d_{x^2-y^2}$) character (see Figure 2b).

For a $[-(H)_3W-N_2-]_n^{n+}$ polymer, with a formal d^2 configuration of the tungsten centers, the π-d band is half filled, so that this species is predicted to show a partial cumulene structure as well as conducting properties. However, for this simple linear system, we expect a pairing Peierls distortion, which would open a band gap at the Fermi level and lead to an alternate $[-W{\equiv}N-N{\equiv}W-N{\equiv}N-]_n^{n+}$ character superimposed on the cumulene structure.

The π-d band is completely filled in the $[-(H)_3W-N_2-]_n^{n-}$ polymer as the tungsten has a d^4 configuration. In such a case, a stable nonconducting species with a cumulene structure is expected to exist. However, this highly anionic species may easily undergo a partial oxidation leading to a conducting doped polymer.

For the neutral $[-(H)_3W-N_2-]_n$ polymer, with a formal tungsten d^3 configuration, the π-d band is three-quarters filled and only a tetrameric distortion is expected to open a band gap at the Fermi level. Since the driving force for the distortion drops off with the size of the distorted unit cell,[12] a lower tendency to Peierls distortion is expected, so that this polymer could show conducting properties.

Our preliminary results anticipate the real possibility of making polymers with relevant physical properties out of dinitrogen.

Experimental Section

2: A THF solution (170 mL) of MesMgBr (188.7 mmol) was added dropwise under N_2 to a suspension of $[WCl_4(dme)]$ (19.6 g, 47.0 mmol) in THF (150 mL) cooled to $-10\,^{\circ}C$. The suspension was stirred and left overnight to warm slowly to room temperature. The resulting red solid (19.0 g) was suspended in toluene and refluxed for 2 h. The final brown-green solution was filtered while hot. The resulting solution was left overnight at room temperature and a crystalline, brown-green solid formed (9.30 g, 29%). ^1H NMR (200 MHz, $[D_6]$benzene, 25 °C, TMS): $\delta = 6.76$ (s, 6H; CH), 6.60 (s, 6H; CH), 2.64 (s, 18H; CH_3), 2.29 (s, 18H; CH_3), 1.98 (s, 18H; CH_3); UV/Vis (toluene): λ_{max} (ε) = 320 nm (18715 $M^{-1}cm^{-1}$); elemental analysis for $\mathbf{2}\cdot C_7H_8$ [%]: calcd $C_{61}H_{74}Cl_2N_2W_2$ (1273.8): C 57.52, H 5.85, N 2.20; found: C 57.50, H 5.96, N 1.67.

The X-ray analysis was performed on green crystals of **4**. A brown THF suspension (400 mL) of $\mathbf{2}\cdot C_7H_8$ (6.40 g, 5.02 mmol) was treated with activated Mg metal (0.174 g, 7.15 mmol). The suspension, stirred overnight under N_2 at room temperature, gave a red solution, which turned deep-violet. The addition of dioxane (50 mL) caused the partial precipitation of $MgCl_2$. The suspension was then filtered. The resulting violet solution was evaporated to dryness and the solid collected with *n*-hexane (100 mL) (4.74 g, 70%). ^1H NMR (400 MHz, $[D_6]$benzene, 25 °C, TMS): $\delta = 6.82$ (s, 6H; CH), 6.66 (s, 6H; CH), 6.52 (s, 12H; CH), 2.60 (s, 18H; CH_3), 2.31 (s, 18H; CH_3), 2.24 (s, 18H; CH_3), 2.11 (s, 36H; CH_3), 1.91(s, 18H; CH_3); UV/Vis (toluene): λ_{max} (ε) = 558 nm (46736 $M^{-1}cm^{-1}$); elemental analysis for $\mathbf{4}\cdot MgCl_2$ [%]: calcd $C_{124}H_{164}Cl_6Mg_3N_6O_8W_4$ (2887.6): C 51.57, H 5.72, N 2.91; found C 51.60, H 5.77, N 2.86.

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