idative quenching of $^*Ru(bpy)_3^{2+}$, rendering the case II mechanism.

(iii) The activation enthalpy and entropy calculated from the Marcus expressions using ΔH_{23} and ΔS_{23}[14] run parallel to the observed ones.[15] Qualitatively, both the **2** → **3** and **3** → **2** processes are explainable within the framework of Marcus theory.

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Multiple Bonds between Transition Metals and Main Group Elements: "Naked" Lead in a Planar Environment[1]

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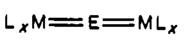
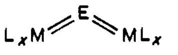
Bare main group elements, surrounded by transition-metal fragments via multiple bonds, are no longer curiosities in organometallic chemistry since several synthetic routes have lately been developed for this class of compounds.[2] To name just two important examples, the unique cumulene-type germanium,[3] tin,[4] and lead compounds[5] of type A are made from monogermane (GeH_4), tin dichloride, and lead dichloride, respectively, while the bent tellurium species B results from treatment of elemental tellurium or tellurium hydride (TeH_2) with a closely related organometallic precursor.[6]


$L_xM{=}E{=}ML_x$

A

L_xM = (η^5-C_5H_5)Mn(CO)$_2$
E = Ge, Sn, Pb



B

L_xM = (η^5-C_5Me_5)Mn(CO)$_2$
E = Te

The central main group elements of such compounds are sterically exposed, thus being centers of high reactivity.[2] We have now achieved the first example of trigonal-planar coordination of the element lead. At this occasion, we demonstrate a further stepwise synthesis of oligonuclear organometallics centering around unsubstituted main group elements.

Treatment of the heterocumulene-type MnPbMn precursor species **1** with an excess of the solvent-stabilized fragment (η^5-$C_5H_4CH_3$)Mn(CO)$_2$ (as THF adduct **2**) at room temperature yields a reaction mixture from which the novel Mn_3Pb compound **3** can be isolated by column chromatography (silica, +15 °C) in ca. 50% yield (Scheme I). This complex crystallizes in black crystals that are not only extremely air-sensitive but can be handled at room temperature only for a brief period of time. Elemental analysis and IR and ^1H NMR spectra established the net formula [(η^5-$C_5H_4CH_3$)Mn(CO)$_2$]$_3$Pb,[7] while a single-crystal X-ray diffraction study at −80 °C confirmed the suggested structure, revealing a strictly planar Mn_3Pb core (Figure 1).[8]

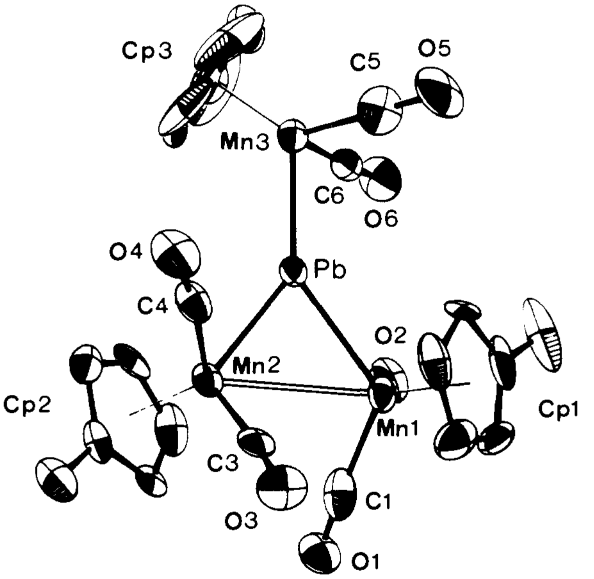
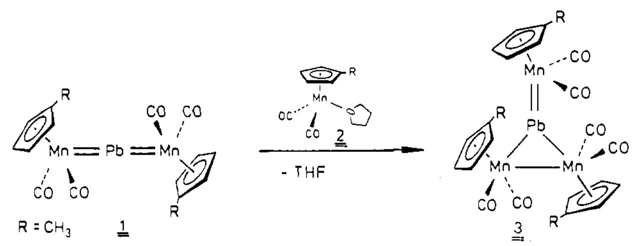


Figure 1. ORTEP representation of the Mn_3Pb compound **3** (−80 °C). Selected bond lengths [pm] and angles [deg]: Mn(1)–Pb 262.0 (1), Mn(2)–Pb 261.1 (1), Mn(3)–Pb 249.0 (1), Mn(1)–Mn(2) 311.0 (1); Mn(1)–Pb–Mn(2) 72.97 (4), Mn(1)–Pb–Mn(3) 143.56 (4), Mn(2)–Pb–Mn(3) 143.41 (4).

Scheme I



The sum of angles around lead amounts of 359.9 (1)°. There are two different types of coordinated (η^5-$C_5H_4CH_3$)Mn(CO)$_2$ fragments: the distances Mn(1)–Pb and Mn(2)–Pb were recorded to be 262.0 (1) and 261.1 (1) pm, respectively, thus being in excellent agreement with single bonds that may be estimated at ca. 261 pm from the elements' covalent radii.[4] To our knowledge, these are the first structurally documented manganese-to-lead single bonds. The Mn(3) fragment, however, is much closer to the central lead atom, with the recorded distance of 249.0 (1) pm being consistent with the formal assignment of a double bond as it results from the EAN rule. Slightly shorter MnPb distances were found in the linear Mn_2Pb skeleton of the precursor species **1** (d(MnPb) = 246.3 (1) pm).[5] A bond length of 311.0 (1) pm between the manganese atoms Mn(1) and Mn(2) suggests metal–metal interaction.[9] The structural data hence support the

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(1) Communication 37 of the series *Multiple Bonds between Transition Metals and Main Group Elements*. This work is being supported by the German Federal Ministry of Research (BMFT), Bonn. Preceeding paper: Herrmann, W. A.; Weichselbaumer, G.; Kneuper, H.-J. *J. Organomet. Chem.* **1987**, *319*, C21.

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(8) Black, triclinic columns grown from dichloromethane/n-hexane at −30 °C, space group $P\bar{1}$ (IT: No. 2), a = 940.3 (1) pm, b = 1177.8 (2) pm, c = 1342.1 (2) pm, α = 67.56 (2)°, β = 78.86 (1)°, γ = 63.96 (1)°, V = 1234 × 10^6 pm^3, Z = 2, $F(000)$ = 740, d(calcd) = 2.093 g·cm^{-3}, μ = 83.32 cm^{-1}, T = −80 ± 1 °C, CAD4 (Enraf-Nonius) Mo Kα radiation, graphite monochromator, ω-scan, $2.0° < \theta < 25°$, $h(-11/11)$, $k(0/6)$, $l(-15/15)$, t(max) = 45 s, number of recorded data 3009, independent reflections 2783, of which 153 unobserved reflections with $I < 1\sigma(I)$ were excluded from refinement. The structure was solved by Patterson methods and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were calculated from ideal positions and included in structure factor calculations: 307 parameter full matrix, R = 0.041, R_w = 0.050; GOF = 3.273. For all calculations the program system STRUX-II was employed. Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting the depository number CSD 52281, the names of the authors, and the journal citation.

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isolobal relationship between the organometallic Mn_3Pb compound **3** and *exo*-methylene cyclopropane: d^6-ML_5 fragments are isolobal with methylene, CH_2.[10]

Whereas the linear Mn_2Pb complex **1** reacts with diazomethane under extrusion of elemental lead and formation of (η^5-$C_5H_4CH_3$)$Mn(CO)_2$(π-C_2H_4), the trigonal-planar Mn_3Pb species **3** polymerizes diazomethane rapidly, but otherwise remains completely unchanged. Further reactivity studies of this class of organometallic "heterocumulenes" are in progress.

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Poly(di-*n*-pentylsilane): The Spectral Consequences of a Helical Conformation in the Solid State

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Polysilane derivatives,[1] which contain only silicon in the backbone, constitute a new class of polymers of scientific interest for which many applications have become apparent.[2-6] Considerable theoretical[7-10] and experimental[11-14] attention has been focused on understanding the nature of the strong electronic transition of the σ-bonded backbone. Recently, however, it was found[15-17] that films of certain polysilane derivatives which are symmetrically substituted with long-chain alkyl substituents [e.g., poly(di-*n*-hexylsilane) (PDHS)] show a remarkable red shift to 370–380 nm. This spectral shift was attributed to the locking of the backbone into a planar zigzag conformation initiated by the crystallization of the hydrocarbon side chains.[15-17] Structural evidence is now presented for poly(di-*n*-pentylsilane) (PDPS) which demonstrates for the first time that deviations of the polymer backbone from a planar zigzag conformation, even in a regular structure, result in a strong blue shift in the electronic absorption spectrum.

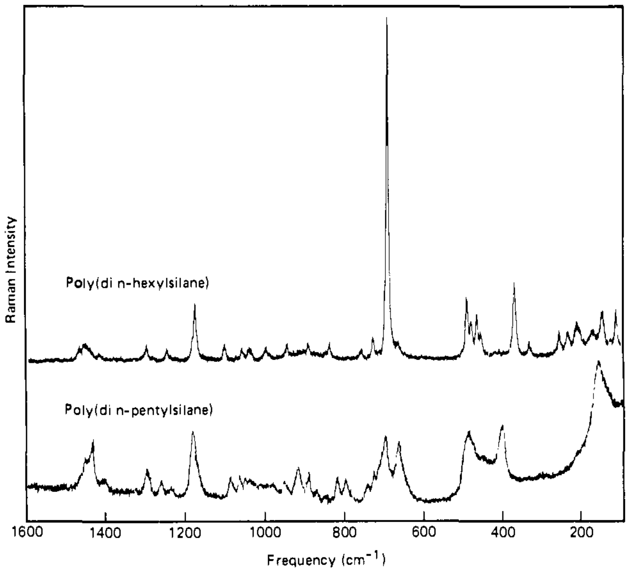

Figure 1. Raman spectra of PDHS (upper) and PDPS (lower). The strong band at 689 cm^{-1} for PDHS has previously been assigned as a carbon–silicon vibration of the planar zigzag backbone conformation based on ^{13}C isotopic labeling studies.

The polymerization of di-*n*-pentyldichlorosilane was performed as previously described.[18] The high molecular weight fraction ($\bar{M}_w \sim 1 \times 10^6$) was isolated by slow precipitation from hexane using isopropyl alcohol. This sample was used in the subsequent spectroscopic studies.

The λ_{max} of a thin film of PDPS at room temperature occurred at 313 nm and appeared similar to the absorption spectra of other amorphous polysilane derivatives *except* that the band was symmetrical and much sharper ($\omega_{1/2} \sim 22$ vs. 50 nm). Upon cooling the film from room temperature to −110 °C, there was little change in band shape or position except for the appearance of a small, broad shoulder around 355 nm. However, when the film was heated above 80 °C, the absorption band broadened significantly ($\omega_{1/2} \sim 58$ nm) although the λ_{max} remained unchanged. This behavior was reversible upon cooling. Thermal analysis of PDPS showed a reversible, endothermic transition around 74 °C ($\Delta H = 0.45$ kcal/mol) which was strikingly different from that observed for PDHS (41 °C, $\Delta H = 5.0$ kcal/mol). Since the transition in the latter case has been attributed to a combination of side-chain melting and the subsequent disordering of a planar zigzag backbone,[15-17] the thermal and UV data for PDPS suggest a regular but nonplanar backbone conformation at ambient temperatures.

Raman studies (Figure 1) demonstrate that the polymer structure of PDPS is significantly different from that of PDHS. Particularly obvious was the absence of a very intense band around 689 cm^{-1} which had previously been assigned[17] as a silicon–carbon vibration in the planar zigzag conformation of PDHS. There are also significant differences in the silicon–silicon stretch region (350–450 cm^{-1}) which indicate that the backbone of PDPS is no longer planar.

The molecular structure of PDPS was further probed by variable-temperature ^{29}Si CPMAS NMR and compared with similar studies on PDHS. The differences in the spectra are striking. Measured at −33 °C, the ^{29}Si resonance of PDPS is significantly upfield from that of PDHS (−29.2 vs. −23.0 ppm, relative to Me_4Si). The observation of a single, relative narrow ^{29}Si resonance ($\omega_{1/2} = 73$ Hz) for PDPS upfield from PDHS further confirms

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