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Unusual NMR Phenomena of Anthracene and Phenanthrene Dianions – Thermal Stimulation of Triplet States in Antiaromatic Systems

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Many aromatic polycyclic benzenoid hydrocarbons undergo a facile reduction process with electropositive metals to yield the corresponding dianions. The $^1\text{H-NMR}$ spectra of some of these doubly charged species exhibit characteristic high-field chemical shifts, which reflect the existence of an enhanced antiaromatic-paratropic ring current^[1-3]. We report here some unusual NMR phenomena which occur in the metal reduction of anthracene **1** and phenanthrene **2** under various conditions.



Anthracene **1** was reduced by adding lithium metal to a THF solution of the hydrocarbon^[1,2]. The blue-green solution of the dianion exhibited a well resolved high-field $^1\text{H-NMR}$ spectrum consisting of an AA'BB' multiplet and a singlet. Over the range -60°C to $+40^\circ\text{C}$ the $^1\text{H-NMR}$ spectrum remained unchanged. No change could be detected in the $^{13}\text{C-NMR}$ spectrum, which is identical with that already reported^[1].

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A different and rather unexpected situation occurs when sodium is used as reducing agent. The $^1\text{H-NMR}$ spectrum of $1^{2\ominus}2\text{Na}^\oplus$ is strongly temperature dependent. At $+40^\circ\text{C}$ the blue solution of the dianion exhibits no signals, whereas at $+20^\circ\text{C}$ three very broad signals at $\delta \approx 3.85$ (2,3,6,7-H), 2.90 (1,4,5,8-H), and 1.65 (9,10-H) are detected. As the temperature was gradually decreased, the signals became markedly sharper. However, even at -60°C the fine structure expected from an AA'BB' system was not observable. The change in line width of the absorptions was reversible, *i. e.* lowering the temperature produced line sharpening. We could not obtain the $^{13}\text{C-NMR}$ spectrum of $1^{2\ominus}2\text{Na}^\oplus$ at room temperature, and even at -30°C the signal/noise ratio was poor.

The same experiment was conducted in a solution of THF and dimethoxyethane (DME) (95:5). At $+20^\circ\text{C}$ the $^1\text{H-NMR}$ signals were much sharper than those exhibited in pure THF at the same temperature. Already at 0°C , the signals at $\delta = 3.9$ and 2.9 exhibited fine structure, and at -30°C the spectrum revealed a well resolved AA'BB' multiplet along with a narrow singlet at $\delta = 1.64$. At this temperature the $^{13}\text{C-NMR}$ signals were similar to those exhibited by $1^{2\ominus}2\text{Li}^\oplus$. As with pure THF, the changes in the NMR spectrum as a function of temperature were completely reversible.

When the reduction was carried out with potassium at -80°C in THF, a $^1\text{H-NMR}$ spectrum could not be recorded for the dianion, even at -20°C . At lower temperatures very broad absorptions at $\delta = 3.8$, 2.9 and 1.6 were found.

Reduction of phenanthrene **2** with sodium in THF to the corresponding dianion did not afford NMR signals over the temperature range -80°C to $+40^\circ\text{C}$. However, reduction with lithium resulted in very broad, high-field $^1\text{H-NMR}$ signals at -30°C . Decreasing the temperature further to -80°C caused line sharpening, but a highly resolved spectrum could not be recorded. Conducting the experiment in THF/DME (95:5) caused further sharpening. The chemical shifts were similar to those already reported [$\delta = 0.5$ (1,8-H), 2.7 (2,7-H), 1.6 (3,6-H), 0.7 (4,5-H), -1.9 (9,10-H)]^[3]. A clear reversibility of the NMR line shapes as a function of temperature was observed.

All these phenomena are strongly related to factors which dominate the ion solvation equilibrium^[4]—highly solvated ion pairs exhibit sharp well-resolved NMR signals, whereas contact pairing results in dramatic line

broadening. Several interpretations are possible, of which the most plausible is based on theoretical considerations which assign a relatively narrow LUMO-HOMO energy gap to antiaromatic species. We presume that the anthracene and phenanthrene dianions are thermally excited triplet state systems in equilibrium with the singlet ground state. At elevated temperatures the excited triplet is highly populated and this results in total disappearance or significant broadening of the NMR signals. Decreasing the temperature causes a relaxation to the singlet ground state as indicated by the observation of NMR signals. This interpretation is consistent with the results of ESR measurements carried out on $1^{2\ominus}2\text{Na}^\oplus$ and $2^{2\ominus}2\text{Na}^\oplus$. The ESR spectra of the frozen THF solutions (-130°C) of $1^{2\ominus}2\text{Na}^\oplus$ and $2^{2\ominus}2\text{Na}^\oplus$ reveal a broad signal centered at 3200 G, along with a sharp signal at 1590 and 1595 G, respectively. The low-field signals are assigned to the $\Delta m_s = 2$ transition, a feature highly characteristic of a triplet state^[5].

The presumed singlet-triplet equilibria are not simple thermal processes but are strongly related to factors which dominate the solution equilibria, *i. e.* nature of the counterion and the solvent^[4].

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A Model Reaction of an Elementary Step in the Fischer-Tropsch Synthesis: $[\text{C}_6\text{Me}_6\text{RuH}(\text{C}_2\text{H}_4)\text{PR}_3]^+$ from $\text{C}_6\text{Me}_6\text{Ru}(\text{CH}_3)_2\text{PR}_3$

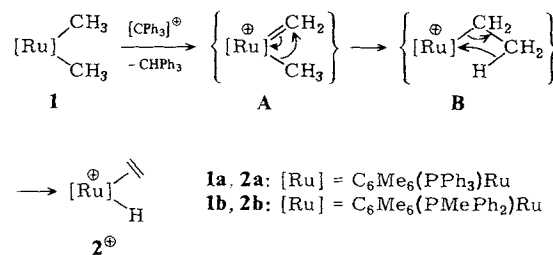
By Heidrun Kletzin, Helmut Werner*, Orhan Serhadli, and Manfred L. Ziegler

Studies of the mechanism of the heterogeneous Fischer-Tropsch synthesis have established that the chain-forming step, *i. e.* the coupling of C—C bonds on the surface of the catalyst proceeds *via* successive insertion of methylene groups into the metal-alkyl bonds^[1a]. Following a β -H elimination, α -olefins are formed as the initial products of the F.T. synthesis.

Model studies, which are based on reactions *in solution* (*i. e.* in a homogeneous phase), have mainly been directed towards the hydrogenation of CO ligands and the insertion of methylene or alkylidene groups into metal-alkyl bonds^[1b]. Maillis *et al.* showed that thermolysis of the dinuclear complex *cis*- $[\text{C}_5\text{Me}_5\text{RhCH}_3]_2(\mu\text{-CH}_2)_2$ produces, apart from methane, mainly ethylene and propene, which can be explained by single and double CH_2 -insertion, respectively, into a Rh—CH₃ bond^[1c]. The *in situ* synthesis of a mononuclear $\text{W}(\text{CH}_2)\text{CH}_3$ complex was achieved by Cooper *et al.*^[1d], who allowed the PF_6 salt of the paramagnetic cation $[(\text{C}_5\text{H}_5)_2\text{W}(\text{CH}_3)_2]^+$ to react with 3-diphenylmethylene-6-triphenylmethyl-1,4-cyclohexadiene (as

source of the trityl radical), and isolated the ethylene(hydrido) complex $[(\text{C}_5\text{H}_5)_2\text{WH}(\text{C}_2\text{H}_4)]^+$ as the major product. In addition to the methyl(methylene) complex $[(\text{C}_5\text{H}_5)_2\text{W}(\text{CH}_2)\text{CH}_3]^+$, a further intermediate $[(\text{C}_5\text{H}_5)_2\text{WC}_2\text{H}_5]^+$ was also postulated.

We have now found that an analogous reaction sequence probably occurs after elimination of a *hydride* ion from a *neutral* (diamagnetic) dimethylmetal compound. Dropwise addition of a solution of $[\text{CPh}_3]\text{PF}_6$ in CH_2Cl_2 to a solution of $\text{C}_6\text{Me}_6\text{Ru}(\text{CH}_3)_2\text{PPh}_3$ ^[2] **1a** in CH_2Cl_2 at -78°C , and subsequent warming to room temperature, leads, after addition of ether, to formation of a colorless, rather air-stable solid. The yield after recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ is 71%. Elemental analysis and spectroscopic data^[3a] confirm the composition $[\text{C}_6\text{Me}_6\text{RuH}(\text{C}_2\text{H}_4)\text{PPh}_3]\text{PF}_6$ **2a**. The analogous reaction of $\text{C}_6\text{Me}_6\text{Ru}(\text{CH}_3)_2\text{PMePh}_2$ **1b** with $[\text{CPh}_3]\text{PF}_6$ in the molar ratio 1 : 1 affords $[\text{C}_6\text{Me}_6\text{RuH}(\text{C}_2\text{H}_4)\text{PMePh}_2]\text{PF}_6$ **2b**^[3a] in 56% yield. We presume that the trityl cation attacks an RuCH₃ group of **1** and eliminates a hydride ion. The initially formed cationic methyl(methylene) complex **A** undergoes CH_2 -insertion (or CH_3 -migration) to give the isomeric coordinatively unsaturated ethyl compound **B**, from which the product **2** is formed by hydride shift from the β -C atom to the metal. That the solvent is *not* involved in the formation of **2a** or **2b** is proved by the synthesis of pure $\text{RuH}(\text{C}_2\text{H}_4)$ cations in CD_2Cl_2 .



The CH_2 -insertion, which mechanistically presumably corresponds to CO-insertion^[4a], should proceed very rapidly according to MO calculations^[4b]. Apart from our findings and those of Cooper *et al.*, the results of Thorn and Tulip^[4c] are also consistent with this. They found that *mer*- $\text{IrBr}_2(\text{C}_2\text{H}_5)(\text{PMe}_3)_3$ is formed from *mer*- $\text{IrBr}(\text{CH}_3)\text{CH}_2\text{OCH}_3(\text{PMe}_3)_3$ and $\text{BrCH}_2\text{OCH}_3$, probably also *via* a cationic $\text{Ir}(\text{CH}_2)\text{CH}_3$ intermediate, which spontaneously rearranges to the isomeric IrC_2H_5 compound.

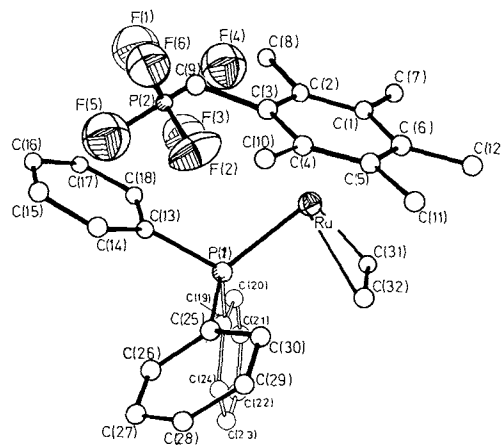


Fig. 1. Structure of **2a** in the crystal. Selected bond lengths [pm]: Ru—P(1) 229.7(2), Ru—C(31) 216.8(10), Ru—C(32) 219.4(9), C(31)—C(32) 141.1(13).

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