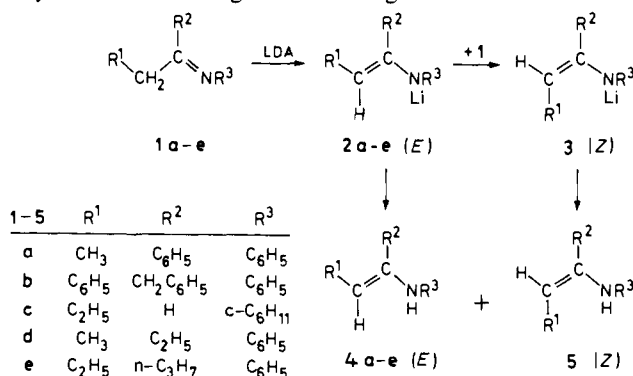


1-Azaallyllithium Reagents (Metalated Schiff Bases). Configurational Equilibration and Stereospecific N Protonation to Metastable *sec*-Enamines¹

Sir:

1-Azaallyl-anion reagents **2** or **3**, prepared by deprotonation^{2,3} of azomethines **1**, are important intermediates in alkylation,²⁻⁵ hydroxyalkylation,³ α -iminoalkylation,⁶ and further reactions.^{7,8} Some of their structural details, although urgently needed for an understanding of enantioselective alkylations,^{9,10} have only recently been studied^{10,11} on isolated examples. C deuteration (back to [²H]-**1**) has been reported;^{4,12} on the other hand, rather unstable *sec*-enamines like **4** or **5** have been obtained by incomplete N protonation of tin and magnesium derivatives of **2/3** with no obvious support for the stereochemical formulations.¹³

We demonstrate now (i) that such anions are configurationally stable with R¹ = alkyl, (ii) that it is possible to equilibrate the two isomers under mild conditions, (iii) that their kinetically terminated N protonation leads almost quantitatively and stereospecifically to *sec*-enamines **4** or **5** of considerable stability, and (iv) that this stereochemical connection may be used for configurational assignments.



The anions **2/3** were generated³ by adding tetrahydrofuran (THF) solutions of **1** to a slight excess of lithium diisopropylamide (LDA) as a base at -70 °C. Metalation occurred rapidly in most cases and the resulting solutions underwent no deterioration or ¹H NMR intensity changes on prolonged standing in stoppered test tubes at room temperature. For example, propiophenone anil **1a** containing 94% *E* isomer¹⁴ was deprotonated to a 3:1 mixture¹⁵ of the anions **2a** and **3a** (*E* and *Z* as shown in the following paragraph). Addition of an excess of methanol to the yellowish-brown solution at -70 °C and immediate ¹H NMR analysis¹⁵ at room temperature revealed the presence of enamines **4a** (*E*) and **5a** (*Z*) in >90% yield and in a 3:1 proportion which hardly changed until both isomers had been converted into the anil **1a** with a half-life of ~ 4 h. The deep red solution containing the anions **2b** and **3b**, obtained in a 1:6 ratio from diphenylacetone anil **1b**, was similarly quenched to yield only a trace of **4b** and predominantly the (*Z*)-enamine **5b** which, however, rearranged rather quickly to **1b**. The stereochemical identification of **4a**, **4b**, and **5a** relies on their spectral identity in dimethyl sulfoxide solutions¹⁶ and the elegant assignments by ¹⁵N coupling constants.¹⁶

The conversion of anions **2/3** into enamines **4/5** with retention of the isomer ratio, which is *not* the thermodynamic ratio in the cases of **4a/5a** and **4b/5b**, for a variety of examples (Table I) is significant and indicates the stereostructure of the educts to be reflected by the products. In connection with the consideration that N protonation does not touch the C=C double bond directly, these observations leave little doubt that **4** is formed stereospecifically from **2**, and **5** from **3**. Hence, the configurational¹⁵ assignments of **2a,b** and **3a,b** become obvious. A direct proof of structural retention is also available from the

Table I. *E/Z* Ratios of 1-Azaallyl Anions **2/3** and of the Corresponding *sec*-Enamines **4/5**^a

structure	2/3				enamines 4 + 5	
	2/3 kinetically controlled		thermodynamically controlled		% NH	<i>t</i> _{1/2} , h
	2:3	4:5	2:3	4:5		
a	75:25	75:25	<5:95	<5:95 ^b	>90	4
b			15:85	<23:77 ^c		<0.1
c			>95:5	>95:5	100	0.5
d	80:20	70:30	<5:95	<15:85	>70	15
e	80:20	60:40	<3:97	<5:95	100	5

^a In THF solution under kinetic and thermodynamic control (see text), with yields and approximate half-lives (*t*_{1/2}) of **4/5** at +25 °C. ^b **4/5** equilibrium ratio <20:80 in Me₂SO solution.¹⁶ ^c **4/5** equilibrium ratio 55:45 in Me₂SO¹⁶ solution (this work).

trans coupling constants in both **2c** and its short-lived *sec*-enamine **4c** (Table I); however, this result is mechanistically less conclusive since **4c** should be the thermodynamically more stable stereoisomer.

Heating of the isomeric mixture of anions **2a/3a** to 60 °C resulted in no change. However, as we deemed it dangerous to accept this as a criterion^{9b,11} of thermodynamic stability, we injected an excess of the anil **1a** as the strongest acid catalyst¹⁷ tolerable in this anion solution. A rather slow but virtually quantitative rearrangement of **2a** to **3a** took place, showing that the original mixture had been generated under kinetic control; upon completion, methanolysis yielded **5a** as a single isomer. The kinetically favored formation of the *E* isomer **3a** lends some support to the proposed¹⁰ deprotonation mechanism; the thermodynamic preference of the *Z* isomer **3a** suggests that the NR³(Li) substituent is "smaller" than the phenyl (R²) group.¹⁸

In probable similarity to hydrazone anions,^{11,19} a very substantial energy barrier against noncatalyzed CC rotation must separate **2** from **3** (except for **2b/3b**), and we believe Table I to present the first clear demonstration that anions of this type may be obtained in their equilibrium ratio. Our results raise the possibility that thermal equilibration of very closely related derivatives^{9b} might have not been complete (unless some azomethine catalyst was regenerated¹⁹ during the reflux period). These conclusions will be of significance for stereoselective syntheses^{9,10} since the prochiral anions **2** or **3** may lead to different products.

E isomers are also preferentially formed from the anils **1d** and **1e** under kinetic control, yielding the pure *Z* isomers **3d** and **3e** by anil catalysis. These assignments¹⁵ are based on chemical-shift comparisons as well as on more general considerations¹⁸ and should be confirmed by independent evidence; however, knowledge of the correct configurations is not relevant for our conclusions on topics i-iii above.

The high yields and kinetic stabilities of *sec*-enamines in protic (excess methanol) but strongly basic solutions are remarkably different from those previously found.¹³ Because of such intermediates, H/D exchange experiments²⁰ may not furnish immediate evidence for the regioselectivity in deprotonation reactions of azomethines. For further synthetic applications¹³ of **4/5**, if prepared by our procedure, the catalytic use⁶ of diisopropylamine is recommended.

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Rudolf Knorr,* Peter Löw

Institute of Organic Chemistry, University of Munich
 Karlstr. 23, D-8000 Munich 2, West Germany

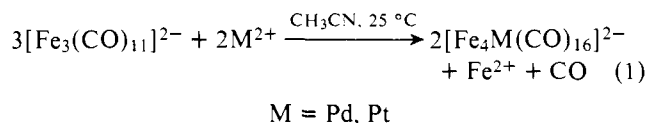
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Synthesis and Characterization of New Fe-Pd and Fe-Pt Carbonyl Anionic Clusters

Sir:

Mixed-metal carbonyl clusters may be useful as starting materials to generate bimetallic crystallites and, furthermore, may provide some insight in their behavior. Since recent work on alloy catalysts pointed out that in heterogeneous catalysis both selectivity and activity may be greatly affected by alloying,¹ extension of the range of known mixed-metal carbonyl clusters^{2,3} is desirable.

We report here our preliminary results on the synthesis and characterization of a series of new Fe-Pd and Fe-Pt carbonyl anionic clusters, viz., [Fe₄M(CO)₁₆]²⁻ (M = Pd, Pt), [Fe₆Pd₆(CO)₂₄H]³⁻, and [Fe₆Pd₆(CO)₂₄]⁴⁻. The two [Fe₄M(CO)₁₆]²⁻ (M = Pd, Pt) dianions have been isolated in high yields (70-80%) as trimethylbenzylammonium (TMBA) salts from the reaction under nitrogen of [TMBA]₂[Fe₃(CO)₁₁] with M(II) salts [MCl₂, K₂MCl₄, (PhCN)₂MCl₂, or (SEt₂)₂MCl₂] in a 1:0.7 molar ratio. The reaction follows the apparent stoichiometry



and, in both cases, the molar ratio is rather critical. Thus, when the amount of Pt(II) salts is increased, the initially formed [Fe₄Pt(CO)₁₆]²⁻ is rapidly converted into a series of more oxidized Fe-Pt carbonyl anions, viz., [Fe₃Pt₃(CO)₁₅]²⁻ and [Fe₄Pt₆(CO)₂₂]²⁻. This reaction is presently under investigation.⁴

On the contrary, in the case of palladium, addition of excess Pd(II) salts results mainly in oxidation of the initially formed [Fe₄Pd(CO)₁₆]²⁻ to Fe(CO)₅ and palladium metal, and there

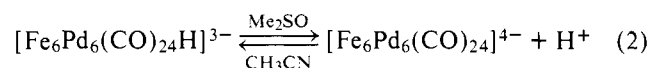
Table I. Infrared Carbonyl Absorptions of the Fe-Pd and Fe-Pt Clusters in CH₃CN Solution

compd	color	ν _{CO} , cm ⁻¹
[Fe ₄ Pd(CO) ₁₆] ²⁻	brown	2035 (vw), 1980 (s), 1970 (s), 1960 (sh), 1940 (ms), 1910 (sh), 1850 (w, br)
[Fe ₄ Pt(CO) ₁₆] ²⁻	brown	2020 (vw), 1985 (s), 1970 (s), 1960 (sh), 1935 (ms), 1925 (sh), 1830 (w, br)
[Fe ₆ Pd ₆ (CO) ₂₄] ⁴⁻	brown	1980 (s), 1950 (sh), 1920 (sh), 1820 (sh), 1800 (m)
[Fe ₆ Pd ₆ (CO) ₂₄ H] ³⁻	green-brown	2005 (s), 1985 (m), 1950 (mw), 1840 (sh), 1825 (m) ^a

^a Very weak ¹H NMR signal in acetone at τ 28.1.

is no evidence of the intermediate formation of the corresponding Fe-Pd carbonyl anionic clusters.

Similar results have been obtained also using different polynuclear carbonyl ferrates, e.g., [Fe₂(CO)₈]²⁻ and [Fe₄(CO)₁₃]²⁻, as starting materials. However, slow reaction (5-10 days) of [TMBA]₂[Fe₄(CO)₁₃] with K₂PdCl₄ (1:1 molar ratio) in THF affords a dark suspension; the red-brown solution contains mainly Fe(CO)₅, [Fe₄(CO)₁₃H]⁻, [Fe₄Pd(CO)₁₆]²⁻, and unreacted [Fe₄(CO)₁₃]²⁻, whereas the dark precipitate (mostly KCl, Fe, and Pd metals) contains small amounts of a mixture of [TMBA]₄[Fe₆Pd₆(CO)₂₄] and [TMBA]₃[Fe₆Pd₆(CO)₂₄H]. Although the yields of these two new products are generally very low (5-10%), the synthesis under these experimental conditions is reproducible, and the stabilization of these two more-oxidized Fe-Pd carbonyl anions is probably the result of the poor solubility in THF of their TMBA salts as well as of K₂PdCl₄. The two salts are slightly more soluble in acetone, acetonitrile, or dimethyl sulfoxide and are reversibly related by the equilibrium



Thus, dissolution either of the mixture or of the hydride derivative in Me₂SO slowly gives rise to formation of the brown [Fe₆Pd₆(CO)₂₄]⁴⁻, which has been isolated in the solid state by addition of excess TMBA⁺Cl⁻ and water. On the contrary, controlled addition of phosphoric acid either to the mixture or to the pure tetraanion in CH₃CN results in separation of tiny black crystals of the less soluble [TMBA]₃[Fe₆Pd₆(CO)₂₄H]. All of these compounds are diamagnetic and their infrared spectra are reported in Table I.

The correct stoichiometry and the molecular structures of [TMBA]₂[Fe₄Pd(CO)₁₆], [TMBA]₂[Fe₄Pt(CO)₁₆], and [TMBA]₃[Fe₆Pd₆(CO)₂₄H]·2CH₃CN have been ascertained by X-ray crystallography.^{5,6} The structures of the two [Fe₄M(CO)₁₆]²⁻ (M = Pd, Pt) dianions are substantially identical and derive from two Fe₂(CO)₈ moieties joined either to a central palladium or platinum atom to give rise to a rectangularly distorted square-planar coordination of iron atoms around the unique central metal atom. When M = Pd (Figure 1), all of the five metal atoms are virtually coplanar, while, when M = Pt, the two Fe₂Pt triangles are slightly twisted and form a dihedral angle of ~7°. Of the four carbonyl groups bonded to each iron atom, three are terminal, while the fourth is bent toward the central metal atom and is better described as semibridging.^{8,9} Since this occurs alternately above and below the metal plane, the four semibridging carbonyl groups give rise to a superimposed tetrahedral coordination of carbon atoms around the central atom. This particular ligand arrangement is not only the result of steric factors,¹⁰ but has also