to give the corresponding olefin in 66% isolated yield (Table I).

The dinuclear chemistry reported here combines two reactions known for mononuclear chemistry: (1) The reaction between an early transition-metal alkylidene and a ketone to give an alkene and a metal-oxo derivative, first noted by Schrock[6] and (2) the recently reported cleavage of the carbonyl bond in the reaction between ketones and $WCl_2(PMe_2Ph)_4$ to give W(6+)-oxo-alkylidene complexes.[7]

Further studies are in progress.[8]

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Multiple Reversible Electrochemical Reduction of Aromatic Hydrocarbons in Liquid Alkylamines

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The thermodynamic reduction potentials of many aromatic hydrocarbons have been known since the work of Hoytink.[1] Their values obtained either by polarographic or by voltammetric techniques have been reported several times in the literature.[2] Recently,[3,4] the further reduction of these species to their respective dianions or higher charged states has attracted increasing interest. The reason is that their electronic and spectroscopic behavior offers new insights into the unconventional properties of charged π-systems. Moreover, highly charged aromatics are interesting model compounds for the study of thermodynamics of charge storage.

Although chemical reduction of such systems is now easily achieved by the reaction with alkali metals, e.g., in dry THF,[3] electrochemical reduction experiments leading to stable higher redox states still demand skill and a sophisticated technique. Therefore, up to now, relatively few reduction potentials for the formation of aromatic diions have been given in the literature. Many are the result of irreversible processes due to protonation reactions induced by impurities in the solvent or by reactivity of the supporting electrolyte.[5] In these cases the desired thermodynamic information cannot be derived from the measured data. Therefore, we will report here on an easily accessible technique of measuring thermodynamic redox potentials of dianions and even higher charged anions of aromatic hydrocarbons using methylamine (MA) and dimethylamine (DMA) as solvents.

In the past, in order to minimize problems arising from coupled chemical reactions, so-called dipolar systems such as acetonitrile (ACN), propionitrile (PrCN), or dimethyl formamide (DMF) have been favored as solvents. Parker et al.[6] showed that by using these solvents and applying a special purification technique with alumina suspended in the cell several aromatic hydrocarbons can be reversibly reduced to their respective dianions within the time scale of slow sweep cyclic voltammetry. This becomes increasingly difficult the more negative the corresponding reduction step occurs on the potential scale. Obviously, the increasing basicity of the diionic or multiionic species as a function of more negative reduction potentials favors successive protonation reactions. In addition, the appearance of background currents normally limits the extension of the cathodic scan to values more positive than −3.0 V vs Ag/AgCl. Therefore, reversible reduction steps at extremely negative potentials around −3.0 V vs Ag/AgCl are exceptional.[7] Since then Heinze et al.[8] have successfully used highly purified and super-dry tetrahydrofuran (THF) with $NaBPh_4$ as supporting electrolyte for the reversible generation of highly charged anions.

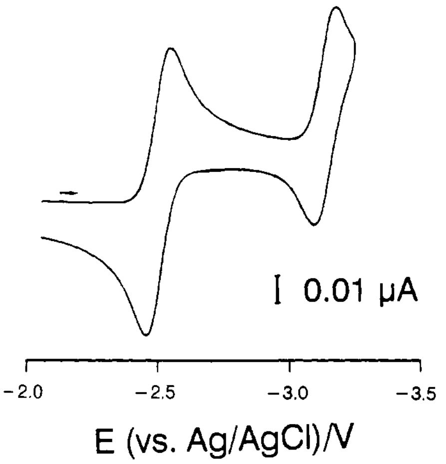

Figure 1. Cyclic voltammogram for the reduction of phenanthrene in DMA/0.1 M TBABr: scan rate = 500 mV s^{-1}; $T = -60$ °C.

In recent years Bard,[9] Savêant, and Thiêbault[10] independent of each other used liquid ammonia as solvent for electrochemical reduction experiments. Because of its extremely low electrophilicity it was possible to determine redox potentials as well as to study reaction mechanisms without side reactions. The cathodic limit of liquid ammonia is −3.0 V vs Ag/AgCl, but the relatively small temperature range of liquidity under normal pressure (mp −78 °C, bp −34 °C) and the insufficient solubility of nonpolar compounds in liquid ammonia limit its use in electrochemistry.

For this reason we used liquid MA and DMA as solvents in cyclic voltammetry for the first time. To our knowledge, only MA has been applied up to now in electrochemistry for electrochemical synthesis and the study of properties of solvated electrons.[11]

MA and DMA stabilize anions to the same extent as ammonia, but in contrast to it they can be used over a larger range of temperatures. The solubility of nonpolar compounds is better and,

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Table I. Redox Potentials of Aromatic Hydrocarbons in DMA/TBABr[a]

	$-E°_1$, V	$-E°_2$, V	$-E°_3$, V	$-E°_4$, V
benzene	3.35[b]			
naphthalene	2.53			
anthracene	2.04	2.64		
phenanthrene	2.49	3.13		
tetracene	1.55	2.15		
azulene	1.62	2.6[d]		
fluoranthene[c]	1.78	2.37		
9-phenylanthracene	1.99	2.55		
9,10-diphenylanthracene	1.98	2.50		
perylene	1.70	2.29		
pyrene	2.13	2.86		
triphenylene	2.42	2.97		
bianthryl	1.915	2.14	2.82	3.165
biphenanthryl	2.35	2.51	3.23[b]	
biphenyl	2.68	3.18		
terphenyl	2.40	2.70		
quaterphenyl	2.28	2.455		
trans-stilbene	2.26	2.72		

[a] Cyclic voltammetry was performed at a Pt electrode (ϕ = 1 mm) with solution 10^{-3}–10^{-4} M in substrate. All redox potentials are determined from the average of the cathodic and anodic peak potentials and are expressed in V vs Ag/AgCl (calibration with $[Cp_2Co]^+/[Cp_2Co]$). T between −40 °C and −65 °C. [b] Cathodic peak potential measured at the rising portion of the background current. The redox potential is determined by digital simulation[14] after subtraction of the background voltammogram. [c] In MA/TBMAI. [d] Irreversible.

finally—the most important aspect—the cathodic limits are shifted to extremely negative potentials, e.g., −3.3 V vs Ag/AgCl for MA and −3.4 V for DMA. By using Pt electrodes, both solvents exhibit a significant low background current density with 2.5 $\mu A/cm^2$ (100 mV s^{-1}), which facilitates measurements at low substrate concentrations too.

The extraordinary qualities of MA and especially DMA in electrochemistry is documented in voltammetric reduction experiments at several simple aromatic hydrocarbons. In most cases—the only exceptions were benzene, naphthalene, and azulene—dianions were generated fully reversible in the time scale of slow sweep cyclic voltammetry. For benzene and naphthalene only a monoanion formation was observed, while for azulene the reduction to the dianion was chemically irreversible. Bianthryl and biphenanthryl could be reduced to their respective tetra- and trianions. The extremely negative redox potentials for the X^-/X^{2-} (X^{2-}/X^{3-}) couples of phenanthrene (Figure 1), triphenylene, pyrene, biphenyl, terphenyl, and biphenanthryl in the presence of tetrabutylammonium bromide as supporting electrolyte were measured for the first time. The redox potential for the reduction of benzene, which has already been published by Heinze and Mortensen,[12] was confirmed. The reduction potentials measured in this study are summarized in Table I.

It should be emphasized that redox potential measurements with tetrabutylammonium salts may differ significantly from those with alkali salts, especially then when higher reduction states are studied. The reason is that alkali counterions shift redox potentials to more positive values due to ion-pairing effects. Furthermore, in most solvents with highly basic di- or multianions tetrabutylammonium cations undergo Hofmann eliminations, which produce protonated followup products. We can only speculate why Hofmann elimination does not occur in these amine solvents. A possible reason is that highly charged anions are well-stabilized, like solvated electrons which have long life-times in liquid ammonia, MA, and DMA. On the other hand, MA and DMA have better donor properties than solvents usually used for reduction experiments, such as THF, HMPA, DMF, and ACN. Thus, a plausible explanation is that the tetraalkylammonium ions are stabilized by the amine solvents.

The experimental technique for the preparation and the use of MA and DMA is simple and resembles, in principle, that reported for liquid ammonia.[9,10] The gas (Messer-Griessheim, 99%) is condensed into a flask containing activated alumina and then refluxed for 1 h to remove all protic impurities. Afterwards it is condensed under vacuum into an electrochemical cell,[13] which allows low-temperature electrochemistry. In order to avoid IR drop problems, small electrodes, e.g., discs with a diameter of less than 1 mm, should be used.

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A Parity Restriction on Dynamic Gearing Immobilizes the Rotors in Tris(9-triptycyl)germanium Chloride and Tris(9-triptycyl)cyclopropenium Perchlorate

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The 9-triptycyl (Tp) groups in molecules of the type Tp_2X (X = CH_2, etc.) undergo virtually unhindered disrotatory cogwheeling in the manner of securely meshed and almost frictionless mechanical bevel gears.[1] Activation energies for this internal motion amount to at most a few kcal mol^{-1}.[2] However, when N meshed gears are arranged in a closed cyclic array, disrotation is possible only if N is even;[3] if N is odd the gears are rigidly locked in place. We now report that the three Tp rotors in each of the title compounds, Tp_3GeCl (**1**) and $Tp_3C_3^+ClO_4^-$ (**2**), are immobilized by this parity restriction on dynamic gearing. To our knowledge, the operation of this mechanical selection rule at the molecular level is without precedent.

Reaction of $GeCl_4$ with TpLi yielded **1**,[4] whose ^{13}C and ^1H NMR spectra[5] are consistent only with a chiral (C_3) conformation in which the three equivalent Tp groups are statically geared.[6] At elevated temperatures there is some line broadening but no evidence of coalescence up to 120 °C (decalin-d_{18}). The lower limit for site exchange and enantiomerization is therefore ca. 20 kcal mol^{-1}. The ^1H and ^{13}C NMR signal patterns of Tp_3SnCl are similar to those of **1**.[7] Tp_3MX compounds of this type exemplify a novel species of molecular propeller[8] in which each

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[2] Conrotation corresponds to gear slippage and requires significantly higher activation energies (e.g., E_a = 33 kcal mol^{-1} for X = CH_2).[1]

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[4] All new compounds were fully characterized by elemental and spectral analyses.

[5] $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, ambient temperature) δ 148.28, 147.53, 146.41, 145.42, 144.08, 143.79 (aromatic quaternary carbons), 130.38, 129.46, 129.24, 125.96, 125.18, 124.97, 123.95, 123.60, 122.91, 122.88, 122.57, 122.48 (aromatic C–H carbons), 78.62 (C(9)), 55.66 (C(10)). ^1H NMR (250 MHz, $CDCl_3$, ambient temperature) δ 9.51 (ddd), 7.43 (ddd), 7.06 (two overlapping ddd's); 8.08 (d), 7.21 (dd), 6.62 (ddd), 5.68 (ddd); 7.77 (d), 7.33 (dd), 6.80 (ddd), 5.90 (ddd) (three sets of four aromatic proton resonances, one for each of the three nonequivalent benzene rings, assigned by NOE difference and COSY experiments—in each set the most downfield proton is the one closest to C(9)); 5.27 (s, H(10)).

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