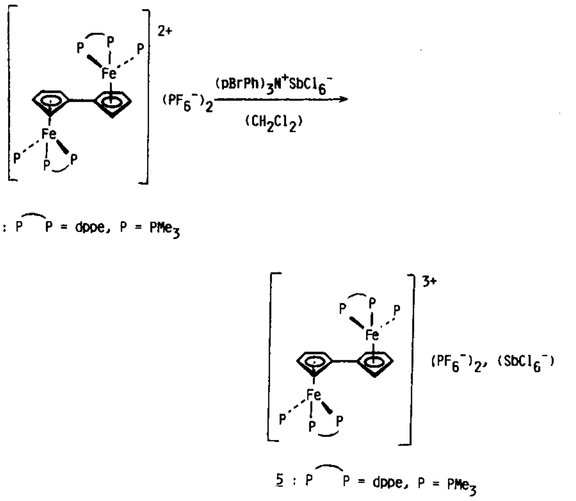
Table II. Compared Mössbauer Data (77 K) of Fe^{II}, $Fe^{II}Fe^{II}$, Fe^{III}, and Mixed-Valence $Fe^{II}Fe^{III}$ Complexes (PF_6 Salts)[a]

	IS (mm s^{-1})	QS (mm s^{-1})
$Fe^{II}Cp(PMe_3)_3{}^+$	0.31	1.87
$Fe_2Fv(dppe)_2(PMe_3)_2{}^{2+}$ (4)	0.35	1.80
$Fe_2{}^{II}Fv(PMe_3)_6{}^{2+}$ (6)	0.32	1.76
$Fe^{III}Cp(PMe_3)_3{}^{2+}$	0.31	0.63
$Fe_2Fv(dppe)_2(PMe_3)_2{}^{3+}$ (5)	0.37	1.37
$Fe_2Fv(dppe)_2(PMe_3)_2{}^{4+}$ (6)	0.38	0.91

[a] All compounds give only one quadrupole doublet. Isomer shifts (IS) are given vs Fe metal, at room temperature. QS = quadrupole splitting.

are observed at −1.90 and −2.00 V vs SCE, and no oxidation wave is observed up to +1.50 V in the CV's. Complex 4 bearing six phosphorus ligands shows two chemically and electrochemically reversible oxidation waves at +0.71 and +0.95 V. Although complex 4 is very insoluble in the common polar solvents, we attempted to oxidize it by using $(p\text{-}BrC_6H_4)_3N^+SbCl_6{}^-$[13] in suspension in dichloromethane (eq 1). Mössbauer spectra of crude samples obtained by



(1)

removal of the solvent under vacuum were made mainly of two quadrupole doublets corresponding to a mixed-valence $Fe^{II}Fe^{III}$ complex, 5 (Table II), and to a $Fe^{III}Fe^{III}$ complex together with signals corresponding to some decomposition to amorphous inorganic Fe^{III}. The Mössbauer spectra of 5 under zero field are essentially temperature independent and show a single quadrupole doublet (Table II), the parameters of which are intermediate between those of $[Fe^{II}Cp(PMe_3)_3]^+(PF_6{}^-)$ and $[Fe^{II}Cp(PMe_3)_3]^{2+}(PF_6{}^-)(SbCl_6{}^-)$, besides traces of unreacted 4 and amorphous inorganic Fe^{III}. That a single quadrupole doublet is found for the $Fe^{II}Fe^{III}$ complex with intermediate parameters between Fe^{II} and Fe^{III} indicates that, on the Mössbauer time scale (10^7 s^{-1}), this compound is a delocalized mixed-valence complex.[14]

Supplementary Material Available: Table of positional parameters, least-squares planes, dihedral angles between planes, distances between atoms, and thermal parameters for 3b (13 pages); a listing of structure factors (14 pages). Ordering information is given on any current masthead page.

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(14) The mixed-valence complex $[Fe_2Fv(PMe_3)_6]^{3+}$ shows electrochemical and Mössbauer data similar to those of 5.[11b]

Selective Catalytic Dehydrogenation of 1,4-Cyclohexadiene to Benzene. 1. Radical Anions Derived from Transition-Metal Arene Complexes as Promoters

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Summary: The reduction of 18e bis(arene) and arene–cyclodiene transition-metal complexes by potassium in dimethoxyethane has been applied to the generation of catalysts for the room-temperature aromatization of 1,4-cyclohexadiene.

Bis(arene)metal sandwiches are usually stable if they do not exceed an 18e count, the bis(hexamethylbenzene) d^7–d^8 group VIII metal complexes[1] being only apparent exceptions because distorsions may occur or the hapticity of one of the ligands may be reduced.

When the arene ligands are monocyclic and the metal possesses six d electrons, the sandwiches are generally inert toward ligand substitution reactions, which are facilitated instead when the system acquires an *extra* electron.[2] Such a labilization of one of the arenes is likely to proceed via the formation of an η^6-arene–η^4-arene complex observed in the case of the reduction of bis(benzene)chromium(0),[3] and this could explain why the bis(arene) d^7–d^8 group VIII metal complexes are rather labile.[1a,4]

These literature data, together with the reactivity of bis(arene) complexes of metals having more than six d electrons toward H–H and C–H bonds,[2,4a,5] have prompted us to pursue aromatic carbon–hydrogen bond activation by introducing an additional electron into neural bis(arene) group VI and arene–cyclodiene group VIII metal complexes. The catalytic aromatization of 1,4-cyclohexadiene under very mild conditions is reported here.

To bis(benzene)chromium(0)[6] (1) (0.36 mmol) and potassium sand (0.41 mmol) were added 1,2-dimethoxyethane, DME (25 mL), and 1,4-cyclohexadiene (5.3 mmol), and the mixture was stirred at 25 °C. This resulted in the total conversion of the diolefin to benzene and dihydrogen (GC);[7] the rate of evolution of the latter under atmospheric pressure increased during the first hour of reaction, reaching a value which corresponded to a turnover of 8.2

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(7) Cyclohexene was found only in trace amounts.

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mol of dehydrogenated substrate per mol of chromium complex per hour and remained constant as long as the substrate was present.

Under the same conditions, bis(benzene)molybdenum(0)[8] (**2**) catalyzed the same transformation, while (benzene)(1,3-cyclohexadiene)iron(0)[9] (**3**) promotes—in an approximate 3:2 ratio—both dehydrogenation and disproportionation to cyclohexene and benzene. The molybdenum and iron complexes or potassium sand do not transform 1,4-cyclohexadiene if contacted individually with it in DME at room temperature.

These results suggest that the presence of an electron in an antibonding orbital (the nineteenth valence electron) is the key feature in the reported catalytic dehydrogenating systems.[10]

From a thermodynamic point of view,[12] dehydrogenation of 1,4-cyclohexadiene to benzene is a favored reaction (ΔG°_{298} may be estimated to be highly negative for the corresponding gas-phase transformation) though it is less favored than disproportionation; benzene and dihydrogen are unstable with respect both to cyclohexene and, a fortiori, to cyclohexane. Accordingly, benzene hydrogenation to cyclohexane is catalyzed at room temperature and atmospheric pressure by an allylcobalt complex;[13] hydroaromatics are catalytically disporportionated to benzene and more hydrogenated hydrocarbons by iridium complexes[14] or iron atoms.[15] On the contrary, catalytic dehydrogenation of hydroaromatics in the absence of a hydrogen acceptor usually requires drastic thermal conditions[16] or irradiation.[17]

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Registry No. **1**, 1271-54-1; **2**, 12129-68-9; **3**, 71265-76-4; 1,4-cyclohexadiene, 628-41-1; benzene, 71-43-2; cyclohexene, 110-83-8; naphthalene, 91-20-3.

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(10) One of the reviewers suggested the possibility that metal particles may be responsible for the observed dehydrogenations. This hypothesis appears to be unlikely for the following reasons: (a) metal formation is to be considered as an endoergonic transformation with respect to any metal complex under the conditions of the experiments; (b) the homogeneous system potassium/naphthalene/DME, in the absence of any added transition-metal complex, promotes the dehydrogenation of 1,4-cyclohexadiene, which is the largely prevailing process, contrary to an earlier report.[11] Diene dehydrogenation and other reactions of dienes promoted by organic radical anions will be reported in a forthcoming publication.

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Book Reviews

Metalloorganicheskaya Khimiya (Metal-Organic Chemistry). Vol. 1. No. 1. Publishing House "Nauka", Moscow. 1988.

We call to the attention of our readers this new bimonthly journal that commenced publication this year. O. A. Reutov of the University of Moscow is the editor-in-chief. He is assisted by an editorial board whose members are I. P. Beletskaya, V. I. Bregadze, M. E. Vol'pin, M. G. Voronkov, L. I. Zakharkin, M. I. Kabachnik, D. N. Kravtsov, V. S. Petrosyan, G. A. Razuvaev, V. I. Sokolov, Yu. T. Struchkov, G. A. Tolstikov, and E. A. Chernyshev. These are well-knwon names within the Soviet organometallic community, and both main-group and transition-metal organometallic chemistry are well represented.

The first issue of 240 pages contains 2 reviews, 38 full papers, 3 brief communications, and 3 letters to the editor. All articles are in Russian, but there is an English translation of the table of contents. It would be most useful to all readers outside the USSR if English translations of the abstracts also were provided.

Organometallic chemistry is a very active field in the USSR, but it is difficult for most of us to keep up with this work. Up until now, most of the Russian organometallic research has been published (in Russian) in three journals: *Izv. Akad. Nauk, Ser. Khim.*, *Zh. Obshch. Khim.*, and *Dokl Akad. Nauk*. If one cannot read Russian, one would have to make do (with some delay) with the synopses in "Chemical Abstracts" or wait (for a long time) for the English translations of these journals. Occasional papers are published in English, principally in the *Journal of Organometallic Chemistry*.

With most of the Russian organometallic papers together in one journal, it will be much easier to keep up with the Russian literature in this field. It is to be hoped that an English translation will be forthcoming.

Like *Organometallics*, *Metal-Organic Chemistry* has chosen blue for its cover. If not the original version, then the English translation, when it becomes available, should be on the shelves of all libraries that serve organometallic chemists.

Dietmar Seyferth, *Massachusetts Institute of Technology*