higher in d character than usual. This high d character induces a bond angle close to 55°, as previously shown by Rappê and Goddard.[34]

The reactivity of $Cl_3MoCH_2^+$ with ethylene was found to be endothermic by 3 kcal/mol, but the empty d orbitals on Mo facilitate olefin coordination and metathesis. Conversely, the reaction of Cl_4MoCH_2 with ethylene was found to be exothermic by 11 kcal/mol. The empty orbitals on Mo, however, are all blocked by the chlorine ligands, and thus coordination of an olefin is sterically encumbered. The thermodynamics of the reaction of $Cl_3MoCH_2^+$ are less favorable than those of the reaction of Cl_4MoCH_2 due to the stronger Mo–C bond strength in $Cl_3MoCH_2^+$.

Acknowledgment. We gratefully acknowledge the National Science Foundation (Grant No. CHE83-18041) for partial support of this research. E.V.A. acknowledges support in the form of a graduate fellowship from Union Carbide.

Registry No. 9, 119970-63-7; 10, 119970-64-8; 11, 83762-89-4; 12, 119970-65-9.

Hydrogen Atom Transfer between μ_2-Ethylidyne Radicals Generated by Electron Transfer: A Novel Disproportionation of a μ_2-Ethylidyne Group to μ_2-Vinylidene and μ_2-Ethylidene

Torill Aase,[1a] Mats Tilset,*[1b] and Vernon D. Parker*[1c]

Institute for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway, the Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway, and the Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

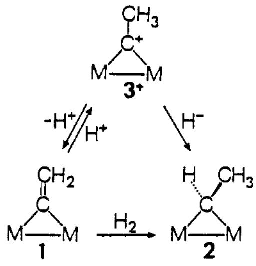
Received December 30, 1988

The bridging ethylidyne complexes $[(\eta^5\text{-}C_5H_5)_2M_2(CO)_3(\mu\text{-}CCH_3)]^+$ (4^+-M, M = Fe, Ru) are reduced electrochemically, or by cobaltocene, in one-electron, chemically irreversible electron-transfer reactions. The initially formed neutral μ_2-ethylidyne radicals undergo rapid decomposition reactions to provide mixtures of bridging vinylidene and ethylidene complexes in good yields. The ratio of ethylidene to vinylidene product yields is highest at high substrate concentrations. The decomposition of the radicals is proposed to take place via competing hydrogen atom loss to the medium and intermolecular hydrogen atom transfer processes between the radicals in a fashion reminiscent of the disproportionation of caged organic radicals.

Introduction

During the last few years, the chemistry of dinuclear hydrocarbyl-bridged transition-metal complexes has received considerable attention.[2,3] Strong impetus for the study of such systems has come from the prospect that they may serve as models for species adsorbed on the surface of heterogeneous catalysts. The recent observation that, on a modified Ru(001) surface, π-bonded ethylene is converted to ethylidyne which subsequently undergoes dehydrogenation to give surface-bonded vinylidene[4] has brought renewed actuality to the study of such model systems and also provides some support for the surface–cluster analogy.[5]

Scheme I



Some widely employed methods for achieving interconversions between μ_2-vinylidene (1), μ_2-ethylidene (2), and cationic μ_2-ethylidyne (3^+) complexes using stoichiometric reagents are depicted in Scheme I. Protonation of 1 yields 3^+[6] in a reaction that may be reversed by the addition of a base (however, protonation may also take place at the α-carbon to yield μ_2-vinyl complexes[7]).

---

(1) (a) University of Trondheim. (b) University of Oslo. (c) Utah State University.

(2) For reviews, see: (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. *Chem. Rev.* **1983**, *83*, 135. (b) Knox, S. A. R. *Pure Appl. Chem.* **1984**, *56*, 81. (c) Hahn, J. E. *Prog. Inorg. Chem.* **1984**, *31*, 205. (d) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171. (e) Casey, C. P.; Audett, J. D. *Chem. Rev.* **1986**, *86*, 339. (f) Albers, M. O.; Robinson, D. J.; Singleton, E. *Coord. Chem. Rev.* **1987**, *79*, 1. (g) Puddephatt, R. J. *Polyhedron* **1988**, *7*, 767.

(3) For some recent leading references, see: (a) Casey, C. P.; Austin, E. A. *J. Am. Chem. Soc.* **1988**, *110*, 7106. (b) Saez, I. M.; Andrews, D. G.; Maitlis, P. M. *Polyhedron* **1988**, *7*, 827. (c) Lewandos, G. S.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1987**, 2703. (d) Herrmann, W. A.; Flöel, M.; Weber, C.; Hubbard, J. L.; Schäfer, A. *J. Organomet. Chem.* **1985**, *286*, 369.

(4) Hills, M. M.; Parmeter, J. E.; Weinberg, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 597, 4224.

(5) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(6) (a) Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023. (b) Forrow, N. J.; Knox, S. A. R. *J. Chem. Soc., Chem. Commun.* **1984**, 679. (c) Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Endesfelder, A.; Knox, S. A. R.; Orpen, A. G.; Plaas, D. *J. Chem. Soc., Dalton Trans.* **1983**, 2661. (d) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Sambale, C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 499. (e) Kao, S. C.; Lu, P. P. Y.; Pettit, R. *Organometallics* **1982**, *1*, 911. (f) Lewis, L. N.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 403. (g) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1985**, 1935.

(7) Al-Obaidi, Y.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319.

0276-7333/89/2308-1558$01.50/0

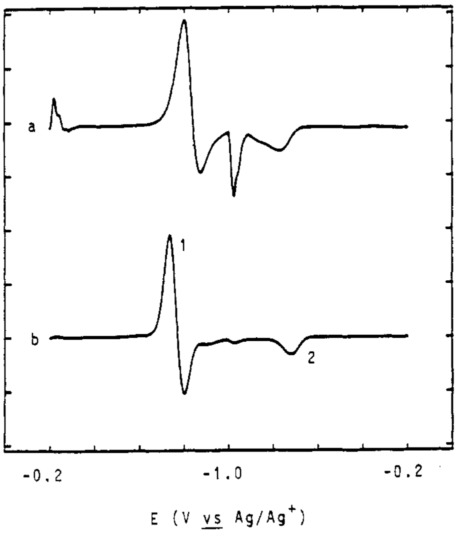


Figure 1. Derivative cyclic voltammogram of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(\mu\text{-}CCH_3)]^+BF_4^-$ (4^+-Fe, 2 mM) in acetonitrile/$Bu_4N^+PF_6^-$ (0.1 M) at a Pt disk electrode (d = 0.6 mm) at 293 K and voltage sweep rates (ν) of (a) 100 V/s and (b) 0.1 V/s.

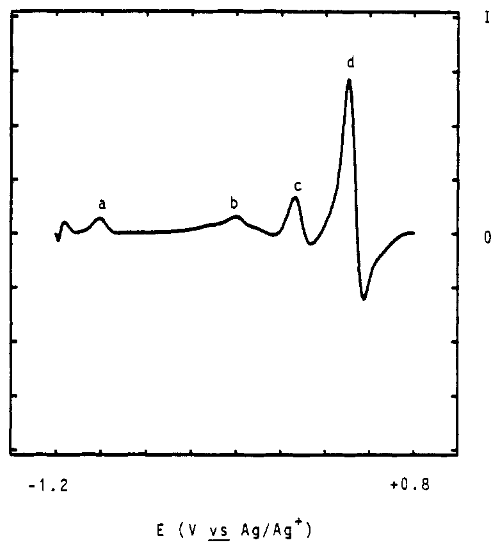


Figure 2. First half of derivative cyclic voltammogram as in Figure 1 at a sweep rate (ν) of 1.0 V/s but initiated during constant potential steady-state electrolysis of 4^+-Fe. Peak a corresponds to the reduction of $4^{\bullet}$-Fe, peaks b and c are unidentified, and peak d arises from the reduction of 5-Fe.

Treatment of 3^+ with hydride reagents provides 2,[6a–c,e,g] whereas hydrogenation of 1 in one case generates 2 directly.[6a]

As part of our ongoing interest in the electron-transfer chemistry of organometallic compounds,[8] we wish in this paper to report the results of an investigation of the reduction chemistry of cationic ethylidyne species 3^+. We will show that compounds of type 3^+ may be converted to 1 and 2 by a simple electrochemical or chemical one-electron reduction followed by a novel disproportionation of the generated radical.

Results

Electrochemical Reduction of $(\eta^5\text{-}C_5H_5)_2M_2(CO)_3(\mu\text{-}CCH_3)]^+$ (M = Fe (4^+-Fe), Ru (4^+-Ru)). The diiron ethylidyne complex 4^+-Fe[6d,9] underwent a chemically irreversible reduction (acetonitrile, 293 K, 0.1 M $Bu_4N^+PF_6^-$, Hg or Pt electrode, substrate concentration 2 mM) at −1.19 V vs the ferrocene/ferricinium couple.[10] Derivative cyclic voltammetry (DCV)[11] traces for this process, recorded at voltage sweep rates (ν) of 0.1 and 100 V/s, are shown in Figure 1. The cyclic voltammetry peak potential corresponds to the point where the rapidly descending DCV curve crosses the base line. The low ratio of the derivative peak currents for the reverse relative to the forward scan (peaks labeled 2 and 1, respectively, in Figure 1) indicated the presence of a rapid follow-up reaction that consumed the electrode-generated intermediate. At ν = 0.1 V/s, the derivative peak current ratio was 0.15, indicating complete reaction on the time scale of the experiment.[12] The peak height on the forward scan was observed to be ca. 90% of that of an equimolar solution of ferrocene, indicating a one-electron process (assuming similar diffusion coefficients for the two).

Unlike 4^+-Fe, the ruthenium analogue 4^+-Ru[6c] was found to undergo extensive deprotonation in acetonitrile/0.1 M $Bu_4N^+PF_6^-$ unless great care was taken to remove traces of moisture from the electrolyte. This reaction took place within 5–10 min, as judged by the gradual disappearance of the DCV signal due to 4^+-Ru and concomitant appearance of an oxidation peak due to vinylidene complex $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3(\mu\text{-}C{=}CH_2)$ (5-Ru) at +0.43 V vs ferrocene/ferricinium. In carefully dried solvent, significant deprotonation could be avoided, and a chemically irreversible reduction wave, similar to that of 4^+-Fe, was observed for 4^+-Ru at −1.38 V vs the ferrocene/ferricinium couple (Hg electrode). The response was not as well-defined for 4^+-Ru as for 4^+-Fe, possibly due to reactions of the electrode-generated radical with the mercury electrode. Repeated scans caused a wave broadening and a decrease in the wave intensity. At a Pt electrode, a broad and featureless signal was observed at ca. −1.2 V vs the ferrocene/ferricinium couple.

Constant current coulometry (Pt gauze electrode) with linear sweep voltammetry (LSV)[11] monitoring of the disappearance of substrate[13] indicated the consumption of 1.0 ± 0.05 faraday/mol both for 4^+-Fe and for 4^+-Ru, establishing overall one-electron reduction processes for both substrates.

A detailed quantitative study of the mechanism of the follow-up reaction by DCV or LSV was thwarted by severe adsorption problems on repeated scans, which caused poor reproducibility in the quantitative measurements. Instead, we had to rely on product studies in order to elucidate the nature and possible mechanism of this reaction.

The immediate decomposition products from the reduction of 4^+-Fe were monitored by DCV as previously reported.[8a,14] Figure 2 shows a DCV scan initiated in the anodic direction from a potential (−1.2 V vs the Ag/Ag^+ reference) at which the radical $4^{\bullet}$-Fe is continuously being generated. On the positive-going sweep, four peaks labeled

---

[8] (a) Tilset, M.; Bodner, G. S.; Senn, D. R.; Gladysz, J. A.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 7551. (b) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *Organometallics* **1987**, *6*, 1628. (c) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 1757.

[9] Nitay, N.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978**, *100*, 3620.

[10] The potentials reported in this paper may be converted to the SCE scale by adding 0.307 V: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1980.

[11] (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem.* **1981**, *121*, 73. (b) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1.

[12] Unlike normal cyclic voltammetry, derivative cyclic voltammetry gives a peak on the reverse scan even in the cases where "complete reaction" of the electrode-generated species takes place on the time scale of the experiment.

[13] Parker, V. D. *Acta Chem. Scand.* **1970**, *24*, 2768.

[14] Bethell, D.; Parker, V. D. *J. Am. Chem. Soc.* **1986**, *108*, 895.

a, b, c, and d are seen. Peak a corresponds to the oxidation of residual $4^{\bullet}$-Fe, while the sources of peaks b and c have not been identified. By comparison with authentic samples, peak d could arise from the oxidation of vinylidene complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(\mu\text{-}C{=}CH_2)$[6d] (**5**-Fe) and/or ethylidene complex $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(\mu\text{-}CHCH_3)$[6e] (**6**-Fe) (vide infra). The oxidation peak potentials for these two species were too close together (+0.24 and +0.23 V vs ferrocene/ferricinium, respectively) for the two to be distinguished if a mixture of the two was at hand. A similar experiment designed to detect the products from reduction of 4^+-Ru was unsuccessful due to severe adsorption problems accompanying the steady-state generation of $4^{\bullet}$-Ru.

Isolation of the products from decomposition of $4^{\bullet}$-Fe and $4^{\bullet}$-Ru, generated by constant current electrolysis of 1.9–2.3 mM solutions of substrates in acetonitrile, was carried out by removal of the solvent after 1.0 faraday/mol had been consumed, extraction with ether and purification by column chromatography (see Experimental Section for details). Thus, reduction of 4^+-Fe yielded vinylidene complex **5**-Fe as the only isolable product (mixture of cis and trans isomers;[15] yield 54%). This establishes that product peak d in Figure 2 arises from **5**-Fe only and that no **6**-Fe was formed in this reaction (the latter was stable to the reaction conditions, as demonstrated by its 92% recovery after electrolysis of a 1:1 mixture of 4^+-Fe and **6**-Fe). On the other hand, reduction of 4^+-Ru under the same conditions yielded vinylidene **5**-Ru[6c] (cis and trans isomers;[15] 60–70% combined) and ethylidene **6**-Ru[6c] (cis and trans; 10–20%). The products **5**-Ru and **6**-Ru were isolated as a mixture, the composition of which was estimated by ^{1}H NMR spectroscopy. We experienced some difficulties achieving complete chromatographic separation of the four different products (including cis and trans isomers) and decided to isolate them as a mixture in order to avoid unnecessary losses during isolation. ^{1}H NMR spectra of the crude reaction mixture and isolated products showed that the relative amounts of **5**-Ru and **6**-Ru did not change during the workup. The relative ratios of products **5**-Ru and **6**-Ru showed some variation from one run to the next. This may reflect the effect of minute amounts of residual water in the electrolyte, which would lead to a higher yield of **5**-Ru relative to **6**-Ru.

The potential hydrogen atom donors and radical traps 9,10-dihydroanthracene, 1,4-cyclohexadiene, and hydroquinone were added to the solutions before electrolysis in attempts at trapping the radicals $4^{\bullet}$-Fe and $4^{\bullet}$-Ru. Reductions in the presence of 9,10-dihydroanthracene were carried out in dichloromethane due to the poor solubility of the trap in acetonitrile. The presence of 1,4-cyclohexadiene and hydroquinone did not affect the relative product yields during the electrochemical reduction of $4^{\bullet}$-Fe. For the reduction of 4^+-Ru, the addition of 9,10-dihydroanthracene or hydroquinone did not significantly alter the relative product yields. The presence of 40 mM of 1,4-cyclohexadiene caused a higher yield of **6**-Ru relative to **5**-Ru. No further increase in the yield of **6**-Ru was seen upon adding more 1,4-cyclohexadiene (this required adding some dichloromethane cosolvent to improve the solubility of the trap). This somewhat puzzling saturation effect may in part be due to the diene forming an emulsion, indicated by the turbid appearance of the solution, at the highest diene concentrations even with the cosolvent addition. Emulsion formation would tend to decrease the effective trap concentration and efficiency in solution. The combined yield of products **5**-Ru and **6**-Ru was not affected to any large extent by the presence of the hydrogen atom donors. Cation 4^+-Ru was unreactive toward 100 mM of 1,4-cyclohexadiene in the absence of a reduction current. Absolute and relative product yields for the electrochemical reduction of 4^+-Fe and 4^+-Ru in the absence and presence of the radical traps are listed in Table I.

Table I. Product Yields and Ratios from the Constant Current Reduction of Ethylidyne Cations 4^+-Fe and 4^+-Ru[a]

substrate[b]	radical trap added	combined product yield,[c] %	5:6 product ratio[d]
4^+-Fe	none	54	>98:2[e]
4^+-Fe	1,4-cyclohexadiene (40 mM)	45	>98:2[e]
4^+-Fe	hydroquinone (40 mM)	57	>98:2[e]
4^+-Ru	none	78	76:24
4^+-Ru	none	77	80:20
4^+-Ru	none	75	81:19
4^+-Ru	1,4-cyclohexadiene (40 mM)	71	65:35
4^+-Ru	hydroquinone (40 mM)	77	80:20
4^+-Ru[f]	none	73	85:15
4^+-Ru[f]	1,4-cyclohexadiene (120 mM)	80	69:31
4^+-Ru[f]	9,10-dihydroanthracene (100 mM)	67	80:20

[a] One-electron reduction in acetonitrile/0.1 M $Bu_4N^+PF_6^-$, unless otherwise noted. [b] Substrate concentrations were 1.9–2.3 mM. [c] Yields of products **5** and **6** isolated as a mixture after column chromatography. [d] By ^{1}H NMR. [e] Trace amounts of **6**-Fe could sometimes be detected by ^{1}H NMR. [f] Dichloromethane solvent.

Cobaltocene Reduction of 4^+-Fe and 4^+-Ru. On the basis of the reduction potentials of 4^+-Fe and 4^+-Ru, cobaltocene ($E° = -1.25$ V vs ferrocene/ferricinium[17]) was expected to be a suitable reagent to effect the chemical reduction of 4^+-Fe and 4^+-Ru. Thus, when acetonitrile-d_3 was added to equimolar amounts of cobaltocene and 4^+-Fe in an NMR tube, the ^{1}H NMR spectrum (only resonances due to the cyclopentadienyl ligands are mentioned here) revealed the presence of the cobalticinium cation (δ 5.65), **5**-Fe (δ 4.86, cis isomer; δ 4.79, trans[15]), **6**-Fe (δ 4.76, cis; δ 4.77 and 4.80, trans), and a trace of ferrocene (δ 4.14). No 4^+-Fe (δ 5.35) remained. The relative yields of **5**-Fe and **6**-Fe were 5:1, and the overall combined yield of the two was 70% (hexamethylbenzene added as an internal standard). The yield of ferrocene was ca. 3%, based on available cyclopentadienyl ligands in 4^+-Fe substrate.

Cobaltocene reduction of 4^+-Ru in acetonitrile-d_3 gave, in addition to the cobalticinium cation, products **5**-Ru (δ 5.32, cis isomer; δ 5.32, trans) and **6**-Ru (δ 5.26, cis; δ 5.26 and 5.28, trans) in a 60:40 ratio.[15] The combined yield in this case was 87% (internal standard). The presence of significant amounts of **6**-Ru was strongly suggestive of the occurrence of an intermolecular hydrogen atom transfer process. In order to obtain further evidence for this assumption, we investigated the reduction of 4^+-Ru-d_3 (85% deuterium in the methyl group) with cobaltocene. The reduction was carried out in nondeuterated acetonitrile, and after the reaction, a small amount of acetonitrile-d_3 was added as an internal reference. The 76.8-MHz ^{2}H NMR spectrum of the product mixture is shown in Figure 3. The signals at δ 6.32 and 6.43 arise from the vinylidene deuteriums in *cis*- and *trans*-**5**-Ru-d_2. Furthermore, the resonances at δ 11.00 and 9.15 are due to the deuteriums in the α-positions and those at δ 2.94 and 3.10 are due to the deuteriums in the β-positions of the ethylidene ligands in *cis*- and *trans*-**6**-Ru-d_4, respectively, by comparison with

---

(15) The dynamics of cis–trans interconversion processes of these and other dinuclear complexes have been studied previously. See ref 6d and 16 for diiron and ref 6c and 16 for diruthenium systems.

(16) Dyke, A. F.; Knox, S. A.R.; Morris, M. J.; Naish, P. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1417.

(17) Kotz, J. C. In *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W. E., Eds.; Plenum Press: New York, 1986; Chapter 3.

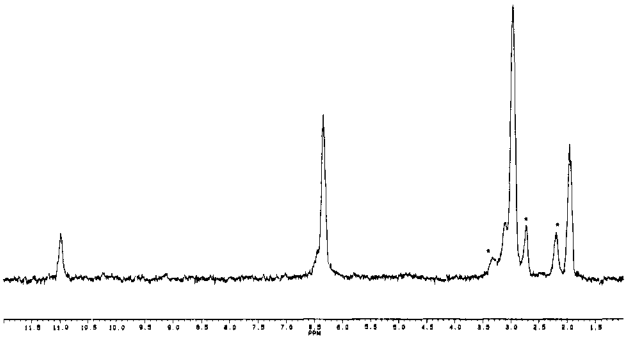


Figure 3. 76.8-MHz ^2H NMR spectrum of the reaction mixture obtained from reduction of 4^+-Ru-d_3 with 1 equiv of cobaltocene in acetonitrile. A small amount of acetonitrile-d_3 has been added as internal standard (δ 1.93).

Table II. Product Yields and Ratios from the Cobaltocene Reduction of Ethylidyne Cations 4^+-Fe and 4^+-Ru[a]

substrate	substrate concn, mM	combined product yield,[b] %	5:6 product ratio
4^+-Fe	0.9	51	>98:2
4^+-Fe	40	54	90:10
4^+-Fe	*d*	70[d]	83:17
4^+-Ru	0.9	75	72:28
4^+-Ru	0.9	*e*	83:17
4^+-Ru	40	77	55:45
4^+-Ru	40	*e*	55:45
4^+-Ru	*d*	87[d]	60:40

[a] All reactions were carried out in acetonitrile at ambient temperature. [b] Isolated yield of mixture of **5** and **6** after column chromatography, unless otherwise noted. [c] By ^1H NMR. [d] Reactions were carried out in NMR tubes. Yields were determined by using hexamethylbenzene as an internal standard. [e] Yield was not determined.

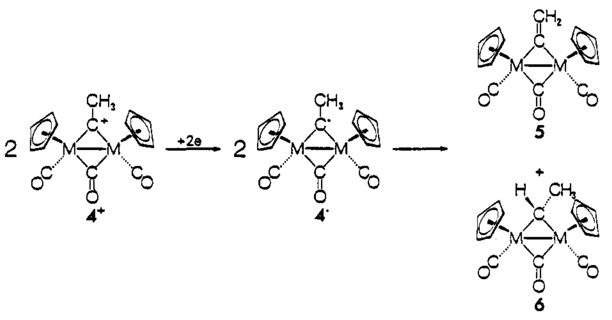
^1H NMR spectra of authentic nondeuterated complexes. The signal at δ 9.15 is hardly observable in Figure 3. However, at the early stages of the acquisition of the ^2H NMR spectrum, this resonance (along with the other attributed to *trans*-**6**-Ru-d_4) was more prominent. The gradual disappearance of these signals may be attributed to the conversion of the trans isomer into the cis isomer.[15] The ^1H NMR spectrum of the product mixture, recorded after the removal of the solvent and addition of acetonitrile-d_3, displayed the expected cyclopentadienyl singlets. Traces of the vinylidene and ethylidene resonances, due to the incomplete deuteration of the methyl group of 4^+-Ru-d_3 substrate, were also observable.

Cobaltocene reductions of 4^+-Fe and 4^+-Ru were also performed on a preparative scale (see Experimental Section for details). These reactions were carried out with both concentrated (40 mM) and dilute (0.9 mM) solutions of the substrates. Relative yields of products **5** and **6**, as well as the combined absolute yields of the two, for the various experiments are included in Table II. It can be seen that dilute solutions gave only traces of **6**-Fe product from 4^+-Fe, whereas a significant amount (up to 28%) of **6**-Ru was formed from 4^+-Ru under similar conditions. Concentrated solutions for both metals provided greater yields of **6**. In fact, the cobaltocene reduction of concentrated solutions of 4^+-Ru yielded a near 1:1 mixture of **6**-Ru and **5**-Ru.

Discussion

The electrochemical experiments, including DCV peak height and constant current coulometry measurements, establish that ethylidyne complexes 4^+-Fe and 4^+-Ru undergo one-electron reduction processes. DCV measurements at 100 V/s indicate that even at high voltage sweeprates, the reduction processes are chemically irreversible due to rapid decomposition of the electrode generated radicals $4^•$-Fe and $4^•$-Ru. Adsorption problems precluded the use of quantitative electrochemical methods to elucidate the kinetics and mechanisms of the decomposition reactions. The instability of these radicals contrasts sharply with the stability of the related thiocarbyne radical $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(\mu\text{-}CSCH_3)$, which has been characterized by IR, UV–vis, and EPR spectroscopy.[18]

Scheme II



The addition of 1 equiv of cobaltocene to solutions of 4^+-Fe and 4^+-Ru led to the complete consumption of the substrates, providing further support for the presence of one-electron reduction processes. The relative yields of products **5** and **6** were dependent on the substrate concentration in these reactions, a finding which is suggestive of intermolecular hydrogen atom transfer reactions between two $4^•$ radicals or between a $4^•$ radical and a 4^+ cation.

The potential hydrogen atom donors hydroquinone, 9,10-dihydroanthracene, and 1,4-cyclohexadiene were added to the electrolyte before preparative electrolyses in attempts at scavenging the radicals. Efficient trapping should favor the formation of products **6** rather than **5**. Only for the electrolysis of 4^+-Ru in the presence of 1,4-cyclohexadiene was a modest increase in the **6**:**5** product ratio observed. It appears that the radicals $4^•$-Fe and $4^•$-Ru are not reactive enough as hydrogen atom acceptors to efficiently abstract hydrogen atoms from the added donors. In contrast, the isoelectronic radical $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2(\mu\text{-}CCH_3)$ ($7^•$), generated from vinylidene complex $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2(\mu\text{-}C{=}CH_2)$ (**8**) and $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, upon its escape from the solvent cage was more effectively scavenged by 9,10-dihydroanthracene, 1,4-cyclohexadiene, or excess $(\eta^5\text{-}C_5H_5)Mo(CO)_3H$, yielding up to 50% of ethylidene complex $(\eta^5\text{-}C_5H_5)_2Co_2(CO)_2(\mu\text{-}CHCH_3)$ (**9**).[6a] Thus, there is precedence for hydrogen atom transfer to bridging ethylidyne radicals, but no evidence for hydrogen atom transfer *between* such radicals has been previously reported. The reason for the difference in reactivities between $7^•$ and $4^•$ toward 9,10-dihydroanthracene or 1,4-cyclohexadiene is not clear.

One might take into consideration two plausible mechanistic alternatives for the hydrogen atom transfer reactions. One option is $H^•$ transfer between two $4^•$ radicals; the other is $H^•$ transfer between a $4^•$ radical and a 4^+ cation. In the following, we will present arguments that suggest that a radical/radical reaction is the more likely pathway. Although the mechanism for the decomposition of $4^•$ to **5** in dilute solution is not known nor is the fate of the hydrogen atom that is lost in this reaction, the fact that this reaction is so facile indicates that the ethylidyne β-

---

(18) Schroeder, N. C.; Angelici, R. J. *J. Am. Chem. Soc.* **1986**, *108*, 3688.

C–H bond in $\mathbf{4}^{\bullet}$ is extremely labile toward homolytic cleavage. On the other hand, the corresponding bond in $\mathbf{4}^{+}$ is not so labile. For example, we observe only very slow reactions (several days), yielding several, and so far unidentified, products upon treatment of $\mathbf{4}^{+}$-Fe or $\mathbf{4}^{+}$-Ru with the triphenylmethyl radical in acetonitrile-d_3. Furthermore, the experimental results indicate that $\mathbf{4}^{\bullet}$-Ru, but not $\mathbf{4}^{+}$-Ru, is capable of abstracting a hydrogen atom from 1,4-cyclohexadiene, at least to some extent. We thus have evidence that radicals $\mathbf{4}^{\bullet}$ are better than cations $\mathbf{4}^{+}$ both as hydrogen atom acceptors and as donors. These findings suggest that a radical/radical reaction is more likely than a radical/cation reaction in the hydrogen atom transfer step.

All our data are most consistent with the mechanism indicated in Scheme II. Initial reduction of $\mathbf{4}^{+}$ generates the radical $\mathbf{4}^{\bullet}$. The radical is short-lived and under dilute conditions readily undergoes loss of a hydrogen atom to the medium. However, at higher concentrations the radical has sufficient lifetime to react with another radical via a hydrogen atom transfer pathway that yields **5** and **6** in a 1:1 ratio. Apparently, relative to Fe, Ru has a stabilizing effect on the β-C–H bond in $\mathbf{4}^{\bullet}$ since hydrogen atom loss to the medium takes place to a much lesser extent from $\mathbf{4}^{\bullet}$-Ru than from $\mathbf{4}^{\bullet}$-Fe. The fate of the lost hydrogen atom under dilute conditions is not known. It is tempting to speculate that the impurity signals labeled (*) in Figure 3 are related to this problem but the lack of corresponding signals in ^{1}H NMR spectra of product mixtures from cobaltocene reduction of $\mathbf{4}^{+}$-Ru appears to discount this possibility. We also considered the alternative explanation that a second cobaltocene molecule could act as a hydrogen atom acceptor toward initially generated $\mathbf{4}^{\bullet}$. Such reactivity has been observed during the reduction of a cationic transition-metal hydride by cobaltocene.[19] However, in our case there was no evidence for formation of the expected cyclopentadiene complex $(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}C_5H_6)$. Other examples of facile homolytic C–H bond cleavage reactions in which the fate of the hydrogen atom is unknown have been reported.[20]

Considering the current interest in the electron-transfer chemistry of mononuclear organometallic compounds, relatively little has so far been reported on the redox properties of dinuclear hydrocarbyl-bridged species. Recent examples of electron-transfer-induced reactivity in such systems include the two-electron oxidative activation of μ-methylene,[21] μ-ethylidene,[21] and μ-vinylidene[22] complexes toward deprotonation, reductive coupling of μ-vinyl cations,[23] and Maitlis' interesting sequence of hydrogen shifts and C–C bond forming reactions during the oxidation of $(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu\text{-}CH_2)_2(CH_3)_2$.[3b,24] The reactions described in this paper provide another example of the interesting redox chemistry of dinuclear systems. We note that the hydrogen atom transfer between two $\mathbf{4}^{\bullet}$ radicals is reminiscent of the disproportionation of caged organic radicals. A possible connection between the reactions reported herein and thermal decomposition reactions of surface-bonded ethylidyne remains to be seen.

Experimental Section

General Data. All manipulations involving organometallic compounds were carried out by using vacuum line, Schlenk, or drybox techniques. Acetonitrile and acetonitrile-d_3 were distilled from P_2O_5 and CaH_2, respectively. The electrochemical instrumentation, cells, data handling procedures, and electrodes have been previously described.[11a,25] Acetonitrile containing 0.1 M $Bu_4N^+PF_6^-$ was used as solvent for electrochemical experiments, and the solution was passed through a column of active neutral alumina before use to remove water and protic impurities. The electrolyte was freed of air by purging with argon, and all measurements were carried out under a blanket of solvent-saturated argon at 293 K. ^{1}H NMR spectra were recorded on a JEOL FX-100 instrument. Chemical shifts are reported in parts per million relative to tetramethylsilane, using the residual solvent proton resonance as internal reference (δ 1.93 for acetonitrile). ^{2}H NMR spectra were acquired on a Bruker AM-500 instrument operating at 76.8 MHz. A small amount of acetonitrile-d_3 was used as the internal reference.

Complexes $\mathbf{4}^{+}$-Fe,[6d] **5**-Fe,[6d] **6**-Fe,[6e] $\mathbf{4}^{+}$-Ru,[6c] **5**-Ru,[6c] and **6**-Ru,[6c] as well as cobaltocene,[26] were prepared according to published procedures.

$[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3(\mu\text{-}CCD_3)]^+$ ($\mathbf{4}^{+}$-Ru-d_3). A solution of $(\mathbf{4}^{+}\text{-Ru})BF_4^-$ (80 mg, 0.15 mmol) in CF_3COOD (1 mL) was stirred for 4 h at ambient temperature. The product was precipitated by the addition of ether (10 mL). The orange powder was washed with ether (4 × 10 mL) and dried in vacuo. The yield was 60 mg (81%, assuming that the counterion was CF_3COO^-). The nature of the counterion was not investigated. The degree of deuterium incorporation into the methyl group was estimated to be 85% by ^{1}H NMR spectroscopy.

Constant Current Coulometry Experiments. Constant current electrolyses were carried out in a H-shaped cell, the compartments of which were separated by a fritted glass junction. A Pt gauze working electrode was used. Electrolysis of solutions of $\mathbf{4}^{+}$-Fe with LSV monitoring of the disappearance of the substrate required the passage of 1.0 ± 0.05 faraday/mol. Cation $\mathbf{4}^{+}$-Fe was found to be stable in the solvent/electrolyte for several hours. However, $\mathbf{4}^{+}$-Ru was found to undergo deprotonation to **5**-Ru (as evidenced by the gradual disappearance of the DCV reduction peak due to $\mathbf{4}^{+}$-Ru) within a few minutes unless great care was taken to keep the solution free of water. When the electrolyte was properly dried, constant current coulometry with LSV monitoring required the passage of 1.0 ± 0.05 faraday/mol for the complete disappearance of $\mathbf{4}^{+}$-Ru.

Preparative Electrolysis Experiments. In a typical experiment, 20 mL of a 2 mM substrate solution of $\mathbf{4}^{+}$-Ru was electrolyzed for the time that was required for the passage of 1.0 faraday/mol of charge. The solutions were concentrated by rotary evaporation, and the neutral products were dissolved by the addition of ether. The filtered extracts were concentrated, and the products were isolated by column chromatography (neutral alumina activity III) using hexane/dichloromethane mixtures as eluents. (Ferrocene, formed during the reduction of $\mathbf{4}^{+}$-Fe, was obtained as a faint yellow forerun that eluted with hexane.) We were unable to achieve complete separation of the four components in the isomer mixtures of **5** and **6** (cis and trans isomers of both) and therefore chose to isolate these as mixtures in order to avoid unnecessary losses during workup. Comparison of ^{1}H NMR spectra of crude reaction mixtures and the isolated products showed that the product ratios had not changed noticeably during workup. Compounds **5** and **6** were the only species detectable by ^{1}H NMR spectroscopy of the purified product mixtures. The product ratios and yields obtained in these reactions are listed in Table I.

Cobaltocene Reduction of $\mathbf{4}^{+}$-Fe and $\mathbf{4}^{+}$-Ru. In a typical experiment for the reduction of dilute solutions of substrate (0.9 mM), a solution of cobaltocene (7.0 mg, 0.037 mmol) in acetonitrile

---

(19) Koelle, U.; Ohst, S. *Inorg. Chem.* **1986**, *25*, 2689.

(20) For example, it was recently reported that an anionic dinuclear cobalt formyl complex underwent homolysis with loss of "H•", yielding a stable dicobalt anion radical: Dumond, D. S.; Richmond, M. G. *J. Am. Chem. Soc.* **1988**, *110*, 7547.

(21) Connelly, N. G.; Forrow, N. J.; Gracey, B. P.; Knox, S. A. R.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 14.

(22) Doherty, N. M.; Fildes, M. J.; Forrow, N. J.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1355.

(23) Casey, C. P.; Austin, E. A. *Organometallics* **1987**, *6*, 2157.

(24) Saez, I. M.; Meanwell, N. J.; Nutton, A.; Isobe, K.; de Miguel, A. V.; Bruce, D. W.; Okeya, S.; Andrews, D. G.; Ashton, P. R.; Johnstone, I. R.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1565.

(25) (a) Ahlberg, E.; Parker, V. D. *J. Electroanal. Chem.* **1981**, *121*, 57. (b) Ahlberg, E.; Parker, V. D. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 97.

(26) Eisch, J. J.; Krug, R. B. *Organomet. Synth.* **1965**, *1*, 65.

(40 mL) was added by syringe to a stirred solution of 4^+-Ru (20 mg, 0.037 mmol) in acetonitrile (40 mL) during a 2-4-min period. The reaction was over immediately, and the mixture of products was isolated following the same workup procedure as for the preparative electrolysis experiments. Reductions of concentrated (40 mM) substrate solutions were carried out analogously, except that the cobaltocene, dissolved in a minimum amount of acetonitrile, was added all at once. Relative and absolute product yields from these reactions are summarized in Table II.

Acknowledgment. We gratefully acknowledge generous support from Statoil under the VISTA program, administered by the Norwegian Academy of Science and Letters.

Communications

Electron Spin Distribution in Cyclotetrasilane Radical Anions

Rudolf Janoschek*,[1a] **and Burkhard Kirste**[1b]

Institut für Theoretische Chemie, Universität Graz
A-8010 Graz, Austria
and the Institut für Organische Chemie
Freie Universität Berlin
D-1000 Berlin 33, West Germany

Received December 7, 1988

Summary: Ab initio PUHF calculations of hyperfine coupling constants of the octamethylcyclotetrasilane radical anion $(Me_2Si)_4^{\bullet-}$ have been performed. A satisfactory agreement with EPR and ENDOR studies could be achieved. The singly occupied MO is composed of Rydberg-like Si-Si pπ and Si-C σ^* contributions.

Cyclopolysilanes are interesting compounds because of their thermal and chemical stability and their unique bonding properties.[2,3] In some respect these saturated compounds resemble aromatic hydrocarbons; evidence of electron delocalization is found in their ultraviolet[4,5] and photoelectron spectra.[5,6] Moreover, peralkylcyclotetra- and peralkylcyclopentasilanes can be reduced to radical anions in which the unpaired electron is delocalized over the ring. These systems have been investigated extensively by EPR[4,7-11] and ENDOR[12] (electron nuclear double resonance) spectroscopy, yielding sets of ^{1}H, ^{13}C, and ^{29}Si hyperfine coupling constants and hence information about the electron spin distribution.

Table I. Spin Density Population (SD), Fermi Contact Analysis (FC in au), and Hyperfine Coupling Constants (*a* in MHz) of Peralkylcyclotetrasilane Radical Anions

	$(Me_2Si)_4^{\bullet-}$				$(t\text{-}BuMeSi)_4^{\bullet-}$
	SD	FC	a_{calcd}[a]	a_{exptl}[b]	a_{exptl}[c]
^{29}Si	0.2618	−0.019 584	+17.39		+15.15
^{13}C	0.0045	0.067 420	+75.78	58.8	+59.07
^{1}H	−0.0035	−0.000 343	−1.53	1.88	+1.45

[a] Calculated with the following proportionality constants (in MHz/au): 4469 (^{1}H), 1124 (^{13}C), and −888 (^{29}Si). [b] From ref 9 and 11. [c] From ref 12.

However, a rigorous quantum-mechanical treatment of cyclosilane radical anions has been lacking so far. A simple perturbation approach was proposed to rationalize the EPR spectra of substituted cyclopentasilane radical anions, leading to a model in which the SOMO (singly occupied molecular orbital) has major contributions from Si-Si σ^* and Si-C σ^* antibonding orbitals involving silicon 3p$_x$, 3p$_y$, and 3p$_z$ and carbon 2s, 2p$_x$, 2p$_y$, and 2p$_z$ atomic orbitals.[11] This model predicts a negative sign for the ^{29}Si hyperfine coupling constant, which is in conflict with the positive sign determined experimentally by TRIPLE resonance.[12] Recently, an ab initio HF-DZP calculation for the hypothetic unsubstituted neutral cyclotetrasilane, $(H_2Si)_4$, has been performed where the LUMO is considered as a model for the SOMO of the radical anion.[13] In the present paper dealing with ab initio PUHF-STO-3G+ calculations[14] for the parent cyclotetrasilane radical anion, $(H_2Si)_4^{\bullet-}$, as well as for the octamethylcyclotetrasilane radical anion, $(Me_2Si)_4^{\bullet-}$, it will be shown that for both systems the SOMO is a Rydberg-like orbital composed of Si-Si π and Si-C/Si-H σ^* contributions (A_{2u} in D_{4h} symmetry).

In Table I a comparison of calculated hyperfine coupling constants of the octamethylcyclotetrasilane radical anion with experimental data for this radical and the related *trans*-1,2,3,4-tetra-*tert*-butyltetramethylcyclotetrasilane radical anion is given. Whereas only an incomplete set of

---

[1] (a) Universität Graz. (b) Freie Universität Berlin.

[2] West, R.; Carberry, E. *Science* **1975**, *189*, 179.

[3] West, R. *Pure Appl. Chem.* **1982**, *54*, 1041.

[4] Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.

[5] Stüger, H.; Hengge, E.; Janoschek, R. *Phosphorus, Sulfur, Silicon*, submitted for publication.

[6] Bock, H.; Ensslin, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 404.

[7] Kira, M.; Bock, H.; Hengge, E. *J. Organomet. Chem.* **1979**, *164*, 277.

[8] Helmer, B. J.; West, R. *Organometallics* **1982**, *1*, 1458.

[9] Wadsworth, C. L.; West, R.; Nagai, Y.; Watanabe, H.; Muraoka, T. *Organometallics* **1985**, *4*, 1659.

[10] Wadsworth, C. L.; West, R. *Organometallics* **1985**, *4*, 1664.

[11] Wadsworth, C. L. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1984. Wadsworth, C. L.; Carlson, C. W.; West, R., private communication.

[12] Kirste, B.; West, R.; Kurreck, H. *J. Am. Chem. Soc.* **1985**, *107*, 3013.

[13] Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6569.

[14] Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Krishnan, R.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA, 1982. The STO-3G basis set is augmented by a diffuse silicon sp set (0.0331) and a diffuse carbon s set (0.0438). D_{4h} symmetry and standard geometry data (pm, deg) have been used: SiSi = 236, SiC = 187, CSiC = 109.

0276-7333/89/2308-1563$01.50/0