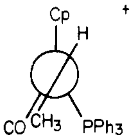
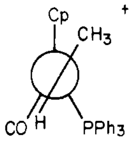
On the basis of stereochemical results observed for the generation of the isomeric $Cp(NO)(PPh_3)Re{=}CHC_6H_5^+$ complexes and the hydride additions to these isomers,[6] it might be anticipated that the two diastereomeric ethers of **3a** would yield carbene complexes of different geometries. Only one species can be observed even when generation from a 1:1 molar ratio of diastereomers is carried out at −95 °C and observed at −90 °C within 10 min. On the basis of the expected low barrier of rotation around the iron–carbon bond in **4a** (< ca. 10 kcal/mol),[11] the lifetimes of the isomers are expected to be quite short. Thus, even if two isomers were generated at −95 °C, isomerization to the thermodynamically favored isomer would probably be quite rapid and preclude observation of the less stable isomer. The close correspondence of chemical shifts of the carbene hydrogen and the lack of coupling between ^{31}P and $^{1}H_{carbene}$ suggest that the ethylidene complex is similar in structure to the analogous benzylidene complex; however, the precise geometry of these complexes is uncertain. Calculations suggest that in such unsymmetrically substituted complexes ($CpLL'M{=}CR_2$) the carbene plane will be twisted from a "vertical" orientation and will be aligned with the Fe–L bond of the better π acceptor.[13] This prediction is supported by the X-ray structure of $CpRe(NO)(PPh_3)CHO$,[20] and such geometries have also been suggested by Gladysz for the two isomers of $Cp(NO)(PPh_3)Re{=}CHC_6H_5^+$.[6] Thus, the two most likely structures for the ethylidene complex are *anti*-**4a** and *syn*-**4a**. On the basis of steric considerations, *anti*-**4a** is likely to be more stable than *syn*-**4a**. The products of decomposition of **4a** have not yet been identified, but clearly the stable ethylene complex $Cp[CO][P(C_6H_5)_3]FeC_2H_4^+$[21] (**5a**) (which could be formed from β-hydrogen migration) is *not* an observed product of decomposition. The relative thermodynamic stabilities of **5a** and **4a** have not been established. However, assuming the ethylene complex **5a** is more stable, the apparent substantial kinetic barrier for hydrogen migration and isomerization of **4a** to **5a** may have its origin in the markedly different coordination geometries preferred by the ethylene and ethylidene ligands.[9-12]



anti-**4a**



syn-**4a**

Immediate ^1H NMR observation at −78 °C of the reaction of **3b** in CD_2Cl_2 with trimethylsilyl triflate reveals neither the ethylidene complex **4b** nor the ethylene complex, $Cp(CO)_2FeC_2H_4^+$ (**5b**). The resultant spectrum has features remarkably similar to those observed from the decomposition of **4a**.[19] However, when this same reaction is carried out in the presence of alkenes, the formation of methylcyclopropanes in high yields provides strong evidence for the presence of the carbene **4b** and demonstrates valuable synthetic potential. In a typical procedure, 1 equiv of styrene and 2 equiv of ether **3b** in CH_2Cl_2 at −78 °C are treated with 2 equiv of trimethylsilyl triflate. The solution is warmed to 25 °C and iron salts are precipitated with pentane. Filtration and solvent removal give the 1-phenyl-2-methylcyclopropane in high yields (91%, cis:trans = 4.7) with traces of unreacted styrene. Table I summarizes results obtained for reaction of several alkenes with **3b**. In all cases, consistently high yields of cyclopropanes can be obtained when a twofold excess of ether **3b** is employed in the reaction. The fact that yields of cyclopropanes drop somewhat when the molar ratio of **3b** to alkene is lowered to 1:1 suggests that the decomposition of carbene **4b** is competitive with addition to the alkene. In accord with this interpretation, when *olefin* is now employed in twofold excess, yields (now based on limiting reagent **3a**) again increase. Consistent with the electrophilic character of the reaction, yields for the more highly reactive alkene, methylenecyclohexane, are less sensitive to the molar ratios used.

On the basis of data in Table I and the ease and economy of the preparation of **3b**, the procedure reported here appears to be the most synthetically attractive one developed to date for transfer of ethylidene. The potentially easy access to ethers of general structure $Cp(CO)_2FeCH(OCH_3)R$ from the corresponding acyl halides (RCOX) points to such complexes as being carbene transfer reagents of very general utility for a wide vaiety of substituents, R. We are currently exploring these reactions as well as use of the optically active acyl complexes $Cp[CO][P(C_6H_5)_3]FeCOR$[22] for use in synthesis of optically active cyclopropanes.

Acknowledgment is made to the U.S. Army Research Office for support of this research.

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Benzoquinone Diimine Bridged Ruthenium Ammines, a Novel Type of Mixed-Valence Complexes

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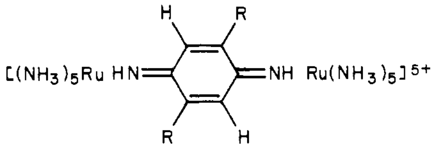
The majority of mixed-valence ruthenium complexes contain nitrogen heterocycles or dinitriles as the bridging ligand.[1] In this communication we report the synthesis and the spectroscopic properties of a novel mixed-valence dimer bridged by *p*-benzoquinone diimine, a molecule which has been shown to form stable complexes with the pentaammineruthenium(II) moiety.[2] The binuclear complex presents further evidence for the high degree of stabilization of the coordinated quinone diimine compared to its uncomplexed state. Moreover, its special features comprising an extraordinarily intense visible absorption and three bands in the near-infrared region are rather unique among mixed-valence ruthenium complexes.

An aqueous solution of $(NH_3)_5RuH_2O^{2+}$ and freshly sublimed 1,4-diaminobenzene in the molar ratio 2:1 was stirred under argon for 1 h. Subsequent oxidation was achieved by bubbling air through this solution, immediately producing an intensely colored blue solution. The blue species was isolated by precipitation with a saturated NaBr solution and purified by chromatography on a Bio-Gel P-2 column. It was identified as the complex ion[3]



1, R = H, CH_3

The most distinctive property of **1** is an extremely intense absorption band at 633 nm (Table I) assigned to a charge-transfer transition. To our knowledge its extinction coefficient of more than 80 000 exceeds those of other ruthenium ammine complexes reported in the literature, indicative of a very strong $t_{2g}(M)$–$\pi^*(L)$ interaction. Upon reduction with Zn/Hg, this band is shifted to 686 nm. Simultaneously, its intensity drops to about 50% of its original value. Reoxidation generates the original position and

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[3] Anal. Calcd for $[(NH_3)_5Ru{-}L{-}Ru(NH_3)_5]Br_5{\cdot}2H_2O$ (L = *p*-benzoquinone diimine): C, 7.88; N, 18.39; H, 4.41; Ru, 22.11; Br, 43.70. Found: C, 7.76; N, 18.13; H, 4.58; Ru, 22.07; Br, 43.0.

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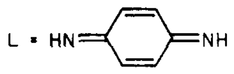
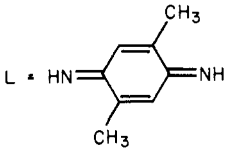
Table I. Visible and Near-Infrared Absorption Bands of $(NH_3)_5Ru\text{-}L\text{-}Ru(NH_3)_5^{5+}$

			
λ, nm	ϵ_{max}	λ, nm	ϵ_{max}
633	88000	643	44200
950, sh		1040, sh	
1355	1040	1400	670
1710	900	1770	800

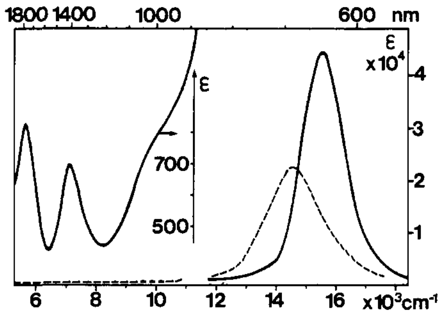


Figure 1. Electronic absorption spectrum (in D_2O) of **1** (R = CH_3, solid line) and its one-electron reduction product (broken line).

intensity. Prolonged action of Zn/Hg causes a steady intensity loss of the 686-nm band. The strong π backbonding of quinone diimine with the $Ru(NH_3)_5$ moiety is also illustrated by the ^1H NMR spectrum of its mononuclear complex with Ru(II). The splitting of the signals for the cis (3.54 ppm) and trans (6.53 ppm) ammonias which gauges this interaction is as large as 3 ppm compared to 1.10–2.10 ppm observed for other $Ru(NH_3)_5L$ species.[4]

In contrast to binuclear mixed-valence ruthenium complexes described so far[1] showing one intervalence band, the near-infrared solution spectrum of **1** exhibits three bands of medium intensity (Figure 1). An identical spectrum was also observed for very thin crystal plates of the $S_2O_6^{2-}$ salt of **1**. Intensity and bandwidth certainly eliminate their assignment to vibrational overtones. Spectroelectrochemical experiments[2] unambiguously classify these bands as an intrinsic property of **1**. The complexes produced by oxidation and reduction of **1** do not show any absorption band in this spectral region. The charge stoichiometry corresponds within 10% to a one-electron reaction for both processes, as verified by the coulometric evaluation of the corresponding cyclic voltammograms. We assign the three near-infrared bands of **1** to intervalence transitions, although a detailed energy level scheme cannot be specified at present. The appearance of three bands instead of one is tentatively attributed to an appreciable tetragonal distortion of the Ru coordination geometry, consistent with the ^1H NMR spectrum of pentaammine(quinone diimine)ruthenium(II). The narrow bandwidths of the order of 1000 cm^{-1} are indicative of considerable valence delocalization in **1**.

The two formal potentials corresponding to the oxidation and reduction of **1** are estimated from conventional cyclic voltammograms as 0.82 and 0.21 V (vs. NHE), respectively.[5] The comproportionation equilibrium is therefore markedly shifted to

$$Ru(II)\text{-}L\text{-}Ru(II) + Ru(III)\text{-}L\text{-}Ru(III) \rightleftarrows 2Ru(II)\text{-}L\text{-}Ru(III)$$

the side of the mixed-valence species **1**, the equilibrium constant K_{com} being 10^{10}. The onset of an irreversible wave in the cyclic

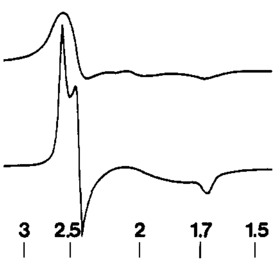


Figure 2. Powder EPR spectra of PF_6 salt of **1** (R = CH_3). Upper trace, 180 K; lower trace, 77 K.

voltammogram around −1 V is associated with the reduction of the ligand quinone diimine to 1,4-diaminobenzene.

We also have to consider the possibility that **1** is not a genuine mixed-valence complex but a Ru(II)–Ru(II) dimer bridged by a Wurster's blue type radical cation. A semiquinone anion bridged Ru(III)–Ru(III) complex is highly improbable considering the position and intensity of the visible absorption band. The EPR spectrum of either species, however, should consist of a signal close to $g = 2$, easily observable at room temperature.[6] A powder sample as well as a solution of **1** (R = CH_3) does not produce any EPR signal at room temperature.[7] We therefore can rule out the presence of an organic radical ion as the bridging ligand and confirm **1** as a mixed-valence complex. Below 200 K an EPR spectrum is observed, the signal line width considerably decreasing with decreasing temperature. The powder spectrum of the PF_6 salt of **1** at 77 K corresponds to $g_{\parallel} = 1.68$ and $g_{\perp} = 2.49$, the latter signal showing an additional rhombic splitting (2.56 and 2.42; Figure 2). A remarkable similarity is observed with the EPR spectrum of the Creutz–Taube complex, where $g_{\perp} = 1.33$ and $g_{\parallel} = 2.63$.[8] When the figures given in ref 8 for the orbital reduction factor ($k = 1$) and the spin–orbit coupling constant ($\lambda = -1050$ cm^{-1}) are used, a tetragonal splitting of 3000 cm^{-1} is estimated for **1**.

Acknowledgment. We thank Professor A. von Zelewsky, University of Fribourg, for measuring the EPR spectra. This work was supported by the Swiss National Science Foundation (Grant 2.427–0.79).

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Formation and Molecular Structure of Bis(η^5-cyclopentadienyl)bis(trifluorophosphine)titanium

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The similarity of PF_3 and CO as ligands was first noted by Chatt[1] in 1950 and subsequently confirmed by Wilkinson,[2] who synthesized the stable complex $Ni(PF_3)_4$ in 1951. Both PF_3 and CO are known to be weak σ donors and strong π acceptors toward transition metals, the stability of a PF_3–metal complex being attributed to strong d_π–d_π interaction between the ligand and the metal.[3-6]

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