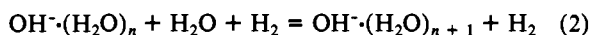


Figure 2. Possible semiquantitative reaction-coordinate profiles for the nucleophilic displacement reaction between OH^- and CH_3Br at various degrees of hydration. The total energies at infinite separation are based on known absolute heats of hydration,¹² and the barrier height ascribed to the transition state in aqueous solution has been taken to be equal to the measured activation energy.⁷ The barrier heights ascribed to the transition state at intermediate degrees of hydration were chosen to be qualitatively consistent with the rate measurements reported in this study.

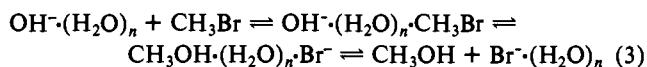
by electron impact on H_2O upstream in a flowing hydrogen plasma at total pressures of ca. 0.4 torr. The hydroxide ions were hydrated by reactions of type 2 and thermalized by collision in the H_2 bath



during the ~ 10 ms available prior to reaction downstream. Partial water vapor pressures were in the range 0.005–2 mtorr. The observations recorded at a fixed water vapor addition upstream and variable additions of CH_3Br into the reaction region are shown in Figure 1. Product ions of the type $\text{Br}^-\cdot(\text{H}_2\text{O})_n$ with $n \geq 2$ were outside the range of detectability of the mass spectrometer. The data for several runs at various additions of water vapor⁹ were analyzed to yield the rate constants summarized in Table I.

The rate constant for reaction 1 is seen to decrease progressively with the stepwise addition of water molecules up to $n = 3$ to a value which represents the present operational limit of our technique. The absolute efficiency of the solvent-free reaction may be estimated to be 0.4 from a comparison of the observed rate constant with the calculated collision rate constant.¹⁰ The total drop in reactivity for hydration of the hydroxide ion up to $n = 3$ observed in the gas phase is almost 4 orders of magnitude. Aqueous solution measurements imply a further drop in reactivity of 12 orders of magnitude (see Table I).⁷

These striking results may be interpreted in terms of the qualitative model discussed by Brauman et al.^{4,5} This model views reactions of this type to proceed in the three-step sequence (3)¹¹



(8) Bohme, D. K.; Hemsworth, R. S.; Rundle, H. W.; Schiff, H. I. *J. Chem. Phys.* 1973, 58, 3504.

(9) The initial relative population of the cluster ions, $\text{OH}^-\cdot(\text{H}_2\text{O})_n$, was dependent on the amount of added water vapor. A wide range in the initial relative populations was desirable for the determination of the rate constants because of losses associated with the depletion of the source ion, $\text{OH}^-\cdot(\text{H}_2\text{O})_{n-1}$.

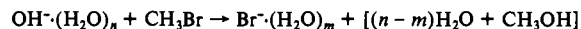
(10) Efficiency is defined as the fraction of the collisions which result in reaction: efficiency = $k_{\text{obsd}}/k_{\text{coll}}$. The collision rate constant may be calculated from the AADO theory: Su, T.; Su, E. C. F.; Bowers, M. T. *J. Chem. Phys.* 1978, 69, 2243.

which may be represented by potential-energy profiles with a double minimum as is done in Figure 2. The efficiency of reaction in the Brauman model results from the trade-off between two effects: (a) differences in entropies of activation between the formation of the transition state and its unimolecular decomposition back to reactants and (b) an energy barrier resulting from the differential solvation of the reactants and the transition state. The former effect is likely to be responsible for the slightly depressed efficiency observed in this study for the solvent-free reaction. The latter effect predominates in solution and accounts for the low reactivity in this medium. An inspection of the rate constants measured in the gas phase suggests that the energy associated with the reorganization of the solvent molecules (effect b) may already predominate at approximately $n = 2$, viz., the energy of the barrier associated with the potential-energy profile for $n = 2$ may be approximately equal to or slightly greater than the energy of the reactants. The observed rate (as well as the calculated reaction efficiency) drops by a factor of about 100 in going from $n = 1$ to $n = 2$ compared to a decrease of only a factor of about 2 in going from $n = 0$ to $n = 1$.

The absolute effect of solvent established by the measurements obtained in this study is likely to be representative of the solvent behavior of $\text{S}_{\text{N}}2$ reactions in general. The relative effects of different solvents which are so pronounced in solution should now also be amenable to measurement in the gas phase. We are therefore faced with the exciting prospect of elucidating a unified model of reactivity for nucleophilic displacement reactions proceeding in the gas phase and solution.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

(11) From a consideration of the overall energetics, it is conceivable that some solvent is "boiled off" according to



In writing this reaction allowance has been made for the possible association of the water and methanol molecules.

(12) (a) Kebarle, P. *Annu. Rev. Phys. Chem.* 1977, 28, 445. (b) Kebarle, P. *Mod. Aspects Electrochem.* 1974, 9, 1-46.

Facile Synthesis, Spectral Characterization, and Ethylidene Transfer Reactions of Complexes of the Type $\text{Cp}(\text{CO})(\text{L})\text{Fe}=\text{CHCH}_3^+$

M. Brookhart* and James R. Tucker

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

G. Ronald Husk

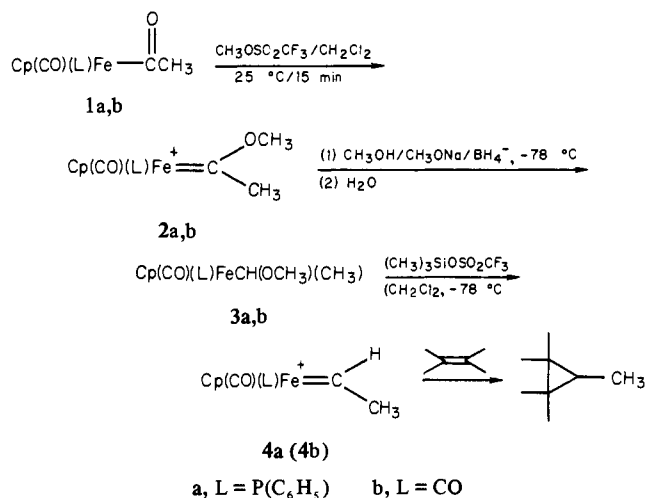
U.S. Army Research Office
Research Triangle Park, North Carolina 27709
Received August 11, 1980

Current routes to alkylcyclopropanes via intermolecular transfer of alkylcarbenes to alkenes are usually limited by low yields, in large measure due to competition from intramolecular rearrangements of the carbene or carbenoid. These isomerizations include, for example, 1,2-hydrogen or -alkyl migrations to give alkenes and insertions into γ and more remote C-H bonds to form cycloalkanes.^{1,2} Observations by Casey³ and Rosenblum⁴ that

(1) For summaries see: (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. (b) Jones, M.; Moss, R. A. *Carbenes* 1973, 1, 1-125.

(2) (a) Simmons, H. E.; Blanchard, E. P.; Smith, R. D. *J. Am. Chem. Soc.* 1964, 86, 1347-1356. (b) Newman, R. C. *Tetrahedron Lett.* 1964, 2541. (c) Kirmse, W. *Angew. Chem., Int. Ed. Engl.* 1965, 4, 891. (d) Kirmse, W.; Wachterhauser, G. *Tetrahedron* 1966, 22, 73-80. (e) The best previously reported procedure for transfer of ethylidene involves use of $\text{CH}_3\text{CH}_2/(\text{CH}_3\text{CH}_2)_2\text{Zn}$: Nishimura, J.; Kawabata, N.; Furukawa, J. *Tetrahedron* 1969, 25, 2647-2659. (f) Kawabata, N.; Yamagishi, N.; Yamashita, S. *Bull. Chem. Soc. Jpn.* 1977, 50, 466-468.

Scheme I



highly electrophilic alkylcarbene transition-metal complexes can rapidly isomerize to olefin complexes suggest that the utility of such complexes as alkylidene transfer reagents may likewise be limited. Further, the few electrophilic alkylidene complexes containing only simple alkyl substituents including Cp(CO)₂M=C(CH₃)₂ (M = Mn, Re),⁵ Cp[NO][P(C₆H₅)₃]Re=CHR⁺ (R = CH₃, CH₂CH₃),⁶ and Cp[(C₆H₅)₂PCH₂CH₂P(C₆H₅)₂]Fe=CHC(CH₃)₃,⁷ have not been reported to react with alkenes. Despite these facts, Casey's report that benzylidene can be transferred from (CO)₅W=CHC₆H₅ to alkenes,⁸ our observations that Cp[CO][L]Fe=CHC₆H₅⁺ [L = CO, P(C₆H₅)₃] transfers benzylidene rapidly and effectively to alkenes and alkynes,¹⁰ and the unique structural aspects of the CpL₂Fe=CHR⁺ systems⁹⁻¹³ (see below) suggested to us that studies of the iron alkylcarbene complexes were warranted.¹⁴ Consequently, we chose complexes of ethylidene, the simplest alkyl-substituted ligand, as the focus for further investigations.

We wish to report here the facile preparation of economically attractive iron ethylidene complexes of surprising stability which exhibit remarkably efficient carbene transfer to alkenes. The

(3) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533-2539.

(4) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354-4355.

(5) (a) Fischer, E. O.; Clough, R. L.; Best, G.; Dreissl, F. R. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 543-544. (b) Fischer, E. D.; Clough, R. C.; Stuckler, P. *J. Organomet. Chem.* **1976**, *120*, C6-C8.

(6) Kiel, W. A.; Lin, G.-Y.; Gladysz, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3299-3301.

(7) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455-2456.

(8) (a) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097-6099. (b) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *Ibid.* **1979**, *101*, 7282-7292.

(9) (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6099-6101. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Organomet. Chem.* **1980**, *193*, C23-C26.

(10) (a) Brookhart, M.; Broom, B. H.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802-7803. (b) Husk, G. R.; Brookhart, M.; Nelson, G. O.; Kratzer, H.; Broom, B.; Tucker, J. IX International Conference on Organometallic Chemistry, Dijon, France, 1979; Abstract B2.

(11) Brookhart, M.; Tucker, J. R.; Flood, T. C.; Jensen, J. *J. Am. Chem. Soc.* **1980**, *102*, 1203-1205.

(12) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585-591.

(13) (a) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592-598. (b) Extended Hückel calculations by R. Hoffmann and O. Eisenstein (unpublished results) indicate that the lowest energy conformations for CpFe(PH₃)₃(NO)(CHCH₃)²⁺ are those in which the ethylidene plane is aligned with the iron-nitrosyl bond.

(14) Several transition metal complexes of the general type L_nM-CH₂X as well as Cp(Ph₂PCH₂CH₂PPh₂)₂Fe=CH₂⁺ have been used as methylene transfer reagents: (a) Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044-5045. (b) Riley, P. E.; Capshaw, C. E.; Pettit, R.; Davis, R. E. *Inorg. Chem.* **1978**, *17*, 408-414. (c) Davison, A.; Krusell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7-C10. (d) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910-1918. (e) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473-6475.

Table I. Reaction of Ethylidene Complex 4b with Alkenes^a

alkene	molar ratio, ^b alkene: 3b	product	yield ^c	isomer ratio
CH ₂ =CHC ₆ H ₅	1:2		91%	4.7:1 (cis:trans)
	1:1		47%	4.7:1
	2:1		75%	4.7:1
	1:2		87%	≥4.5:1 (syn:anti) ^d
	1:1		25%	≥4.5:1
	2:1		60%	≥4.5:1
	1:2		99%	
	1:1		67%	
	2:1		86%	

^a Reactions carried out as described in text. ^b In all reactions the molarity of 3b was held constant (0.35 M). ^c Calculated by using GLC results calibrated with an internal standard. Yields based on the limiting reagents in all cases. ^d Based on an observed *cis*-cyclopropane coupling $J_{\text{H}_1-\text{H}_2} = J_{\text{H}_3-\text{H}_4} = 8.5$ Hz for the major isomer (250-MHz decoupled spectra).

reactions summarized in Scheme I represent a viable new route to methylcyclopropanes which may prove general for a wide variety of alkylcyclopropanes.

Alkylation of the readily available acetyl complexes¹⁵ (1a,b) with methyl triflate in methylene chloride proceeds rapidly and quantitatively to generate the methoxycarbene complexes 2a and 2b. Hydride addition to 2a and 2b is accomplished by quenching the methylene chloride solutions of these ions into CH₃OH/CH₃ONa/BH₄⁻ at -78 °C. Dilution with water followed by extraction with methylene chloride gives the spectroscopically pure ethers 3a and 3b in excellent yields (95% and 89%, respectively).¹⁶⁻¹⁸ No overreduction to the ethyl derivative, Cp[CO][L]FeCH₂CH₃, is observed in either system.¹⁷ In the case of 3a, a mixture of two diastereomers (ca. 1:1 molar ratio) is noted.¹⁶

Treatment of 3a (either diastereomer) with trimethylsilyl triflate in CD₂Cl₂ yields quantitatively a solution of the triflate salt of the ethylidene complex 4a. The ¹H NMR spectrum of 4a at -78 °C shows a methyl doublet at δ 2.84 ($J = 7.8$ Hz), C₅H₅ at 4.34 (5 H, $J_{\text{3p-1H}} = 2$ Hz), an aromatic multiplet centered at δ 7.18-7.80 (15 H), and, most characteristic of highly electrophilic carbene complexes,^{6-9,11} a quartet at δ 17.94 ($J_{\text{H-CH}_3} = 7.8$ Hz) for the proton bound to the carbene carbon. Remarkably, complex 4a is moderately stable in solution at 25 °C ($t_{1/2} \sim 3$ h).

(15) (a) Bibler, J. P.; Wojcicki, A. *Inorg. Chem.* **1966**, *5*, 889-892. (b) Green, M. L. H.; Mitchard, L. C.; Swanwick, M. G. *J. Chem. Soc. A* **1971**, 794-797.

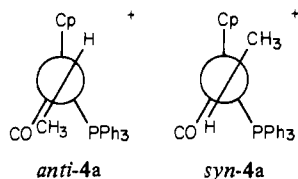
(16) Spectroscopic data for 3b: ¹H NMR (C₆D₆) δ 1.85 (CH₃, d, $J = 6$ Hz), 3.23 (OCH₃, s), 4.30 (C₅H₅, s), 4.94 (H_{ar}, q, $J = 6$ Hz); ¹³C NMR (C₆D₆) δ 33.1 (CH₃), 58.3 (OCH₃), 80.4 (CH), 87.2 (C₅H₅), 217.9, 219.0 (diastereotopic CO's); IR (CH₂Cl₂) ν_{CO} 1944, 1996 cm⁻¹. Data for 3a (diastereomer A): ¹H NMR (C₆D₆) δ 1.89 (CH₃, dd, $J_{\text{HH}} = 6$ Hz, $J_{\text{PH}} = 1.8$ Hz), 3.03 (OCH₃, s), 3.95 (H_{ar}, m), 5.45 (C₅H₅, d, $J_{\text{PH}} = 1.6$ Hz), 7.0-8.0 (C₆H₅, m); ¹³C NMR (C₆D₆) δ 29.1 (CH₃), 58.1 (OCH₃), 81.1 (CH, d, $J_{\text{13C-31P}} = 22$ Hz), 85.6 (C₅H₅), 126-138 (aromatic carbons, PPh₃), 222.2 (CO, d, $J_{\text{13C-31P}} = 32$ Hz); IR (CH₂Cl₂) ν_{CO} 1898 cm⁻¹. Data for 3a (diastereomer B): ¹H NMR (C₆D₆) δ 1.91 (CH₃, d, $J_{\text{HH}} = 6$ Hz), 3.35 (OCH₃, s), 3.95 (H_{ar}, m), 5.41 (C₅H₅, d, $J_{\text{PH}} = 1.6$ Hz), 7.0-8.0 (C₆H₅, m); ¹³C NMR (C₆D₆) δ 31.6 (CH₃), 57.9 (OCH₃), 80.7 (CH, d, $J_{\text{13C-31P}} = 18$ Hz), 85.6 (C₅H₅), 126-138 (aromatic carbons, PPh₃), 223.5 (CO, d, $J_{\text{13C-31P}} = 32$ Hz); IR (CH₂Cl₂) ν_{CO} 1898 cm⁻¹.

(17) Davison and Reger have prepared the ethoxy analogue of 2a via ethylation of 1a. Reduction of the ethoxy carbene with NaBH₄ in ethanol gave the two diastereomers of the ethyl ether Cp(CO)[P(C₆H₅)₃]FeCH(CH₃)-OCH₂CH₃ as well as substantial amounts (ca. 50%) of Cp(CO)[P(C₆H₅)₃]FeCH₂CH₃: Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9238-9239. Green^{15b} has also reported a similar borohydride reduction of the ethoxy analogue of 2a.

(18) Complex 3b has recently been reported by Cutler through alkylation of 2b with dialkoxycarbene salts and reduction with Cp(CO)(Ph₃P)FeH: Bodnar, T.; LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 3292-3294.

(19) In CD₂Cl₂ solution at 25 °C, ethylidene complex 4a slowly decomposes. A new major C₅H₅ band appears at δ 5.3 and a band which shows considerable fine structure grows in at δ 0.5-2.0. No characterizations of these species have yet been made, but the high-field band is suggestive of formation of cyclopropanes.

On the basis of stereochemical results observed for the generation of the isomeric $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}=\text{CHC}_6\text{H}_5^+$ 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** ($< \text{ca. } 10 \text{ kcal/mol}$),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 $^1\text{H}_{\text{carbene}}$ 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 ($\text{CpLL}'\text{M}=\text{CR}_2$) 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 $\text{CpRe}(\text{NO})(\text{PPh}_3)\text{CHO}$,²⁰ and such geometries have also been suggested by Gladysz for the two isomers of $\text{Cp}(\text{NO})(\text{PPh}_3)\text{Re}=\text{CHC}_6\text{H}_5^+$.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 $\text{Cp}[\text{CO}][\text{P}(\text{C}_6\text{H}_5)_3]\text{FeC}_2\text{H}_4^{+21}$ (**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

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, $\text{Cp}(\text{CO})_2\text{FeC}_2\text{H}_4^+$ (**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 $\text{Cp}(\text{CO})_2\text{FeCH}(\text{OCH}_3)\text{R}$ from the corresponding acyl halides (RCOX) points to such complexes as being carbene transfer reagents of very general utility for a wide variety of substituents, R. We are currently exploring these reactions as well as use of the optically active acyl complexes $\text{Cp}[\text{CO}][\text{P}(\text{C}_6\text{H}_5)_3]\text{FeCOR}^{22}$ for use in synthesis of optically active cyclopropanes.

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

(22) Brunner, H.; Schmidt, E. *J. Organomet. Chem.* 1973, 50, 219-225.

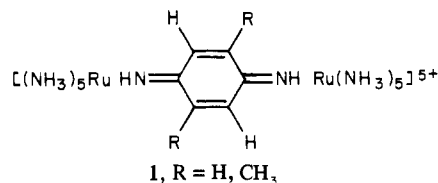
Benzoquinone Diimine Bridged Ruthenium Amines, a Novel Type of Mixed-Valence Complexes

Stefan Joss, Heinz Reust, and Andreas Ludi*

*Institut für Anorganische Chemie
Universität Bern, CH-3000 Bern 9, Switzerland
Received August 28, 1980*

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 $(\text{NH}_3)_5\text{Ru}_2\text{O}^{2+}$ 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 ion³



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 80000 exceeds those of other ruthenium ammine complexes reported in the literature, indicative of a very strong $t_{2g}(\text{M})-\pi^*(\text{L})$ 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

(1) Taube, H. *Ann. N.Y. Acad. Sci.* 1978, 313, 481.

(2) Rieder, K.; Hauser, U.; Siegenthaler, H.; Schmidt, E.; Ludi, A. *Inorg. Chem.* 1975, 14, 1902.

(3) Anal. Calcd for $[(\text{NH}_3)_5\text{Ru}-\text{L}-\text{Ru}(\text{NH}_3)_5]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (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.

(20) Wong, W.-K.; Tam, W.; Strouse, C. E.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* 1979, 530.

(21) Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* 1972, 94, 9238-9239.