The nmr spectra of **3** and its acetyl derivative **9**, taken at several temperatures, are shown in Figure 1. A comparison of the spectra fails to reveal any marked difference in the temperature dependence of proton averaging for the three magnetically nonequivalent protons whose chemical shift differences are virtually identical for the two compounds. These results are clearly not in accord with a transition state for bond migration of the form **1** or **2** in which appreciable positive charge is developed on the metal atom. They are, however, consonant with the view that reaction occurs by way of an essentially nonpolar transition state, as has been depicted for sigmatropic rearrangements.[9]

The great facility with which these rearrangements occur, contrasted with the very much higher activation energies associated with [1.5] sigmatropic shifts of C–H bonds in substituted cyclopentadienes,[10] is most reasonably attributed to the relatively low bond energy of the Fe–C bond[11] and possibly as well to the more diffuse character of the metal orbital constituting the metal–carbon bond which would be expected to facilitate its continuous overlap with the cyclopentadienyl π orbitals in the course of the rearrangement.[12,13]

Acknowledgment. We are indebted to Dr. G. Dudek for allowing us to use the facilities at Harvard University for some of the low-temperature measurements. This research was supported by National Institutes of Health Grant GM 05978 which is gratefully acknowledged.

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[9] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

[10] W. R. Roth, *Tetrahedron Letters*, **17**, 1009 (1964); S. McLean and P. Haynes, *ibid.*, **34**, 2385 (1964).

[11] Measured with respect to a d^8 valence state, the Fe–C bond in Fe(CO)$_5$, which is of greater bond order than 1, is estimated to have a mean bond dissociation energy of 58.6 kcal/mol: H. A. Skinner, *Advan. Organometal. Chem.* **2**, 49 (1964). The mean bond dissociation of this bond with respect to ground-state Fe is estimated as 28 kcal/mol: F. A. Cotton, A. K. Fischer, and G. Wilkinson, *J. Am. Chem. Soc.*, **81**, 800 (1959); Fritz and Kreiter[4] had also noted the importance of the low carbon–metal bond energies in σ-cyclopentadienyl complexes in promoting rearrangement.

[12] The very great dependence of the rate of these rearrangements on the bond energy of the sigmatropic bond is well documented for the [3.3] sigmatropic rearrangements of *cis*-divinylcyclopentane, -cyclobutane, and -cyclopropane: W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 720 (1963); E. Vogel, *Ann.*, **615**, 1 (1958); E. Vogel, W. Grimme, and E. Dinné, *Angew. Chem.*, **75**, 1103 (1963).

[13] Both σ-C$_5$H$_5$CuP(C$_2$H$_5$)$_3$[3] and (σ-C$_5$H$_5$)Hg[14] are reported to exhibit an apparent increase in the rate of sigmatropic rearrangement in the presence of Lewis bases such as triethylamine. These effects, which are not observed for **3**, appear to be due to coordination of the metal by the base. Whether or not the consequence of such coordination is to promote stabilization of a dipolar transition state, as has been suggested,[3] or results simply in a weakening of the metal–carbon bond, the symmetry requirements for the rearrangements would be expected to be unaltered.

[14] E. Maslowsky and K. Nakamoto, *Chem. Commun.*, 257 (1968).

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Formation of an Unstable Dinitrogen Complex of Ruthenium(II)

Sir:

Recently a dinitrogen complex of osmium(II), *cis*-[Os(NH$_3$)$_4$(N$_2$)$_2$]Cl$_2$, was reported, as was the failure to make an analogous complex of ruthenium(II).[1] We wish to report the formation of unstable [Ru(en)$_2$(N$_2$)$_2$]$^{2+}$ by means of reaction 1. Previous attempts to prepare

$$cis\text{-}[\mathrm{Ru(en)_2N_3N_2}]^+ + \mathrm{HNO_2} \xrightarrow[\text{cold}]{} cis\text{-}[\mathrm{Ru(en)_2(N_2)_2}]^{2+} + \mathrm{N_2O} \quad (1)$$

metal–nitrogen complexes by the reaction of metal–azido compounds with nitrous acid were not successful.[2,3]

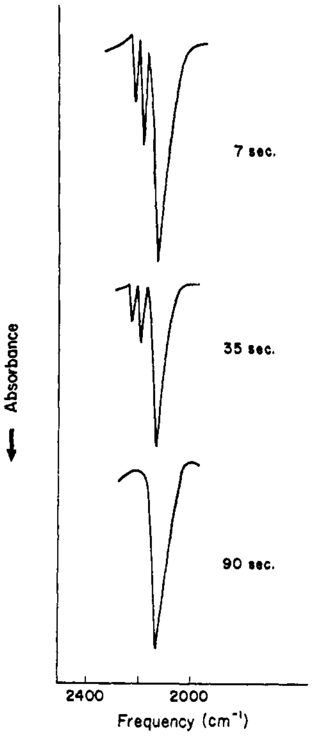

Figure 1. The infrared spectra of samples isolated after various periods from the reaction of nitrous acid on *cis*-[Ru(N$_3$)(N$_2$)en$_2$]$^+$.

Reaction 1 is extremely rapid even at 0°. The immediate (~7 sec) addition of a cold solution of NaB(C$_6$H$_5$)$_4$ to the reaction mixture results in the coprecipitation of the salts *cis*-[Ru(en)$_2$(N$_2$)$_2$][B(C$_6$H$_5$)$_4$]$_2$ and *cis*-[Ru(en)$_2$H$_2$O(N$_2$)][B(C$_6$H$_5$)$_4$]$_2$. Figure 1 shows the N–N stretching region of the ir spectra for such mixtures collected at various times. The bands at 2220 and 2190 cm^{-1} are assigned to the *cis*-dinitrogen complex, in accord with the two bands reported[1] for *cis*-[Os(NH$_3$)$_4$(N$_2$)$_2$]Cl$_2$. Also in agreement with this assignment is the observation that these bands decrease in intensity with increasing isolation time. Furthermore, in the solid state at room temperature the bands gradually disappear in about 30 min. These results show that a metal–nitrogen compound is formed by the reaction of a metal–azido complex with nitrous acid and that the dinitrogen complex *cis*-[Ru(en)$_2$(N$_2$)$_2$]$^{2+}$ is not very stable. If π bonding of the type $\mathrm{Ru} \rightleftharpoons \mathrm{N}{=}\ddot{\mathrm{N}}\colon$ is important in these systems, then it is reasonable that two nitrogens would have to share in such bonding and be held less firmly than in a corresponding system containing only one nitrogen. In agreement with this is the observation that the N–N stretching frequencies are higher for the dinitrogen complex *cis*-[Ru(en)$_2$(N$_2$)$_2$]$^{2+}$ (2220 and 2190 cm^{-1}) than for the mononitrogen cation *cis*-[Ru(en)$_2$H$_2$ON$_2$]$^{2+}$ (2130 cm^{-1}). Likewise the latter

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[1] H. A. Scheidegger, J. N. Armor, and H. Taube, *J. Am. Chem. Soc.*, **90**, 3263 (1968).

[2] R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

[3] T. Studer, private communication.

complex in aqueous solution does not react with N_2 to give the dinitrogen compound, whereas $[Ru(NH_3)_5H_2O]^{2+}$ does react with N_2 to yield the mononitrogen compound.[4]

The dinitrogen and the aquonitrogen complexes were prepared by mixing at 0° an aqueous solution (2 ml, 0.000038 mole) of *cis*-$[Ru(en)_2N_2N_3]PF_6$ with a freshly prepared solution (5 ml, 0.000038 mole) of HNO_2. Immediate vigorous gas evolution occurred, and the solution color changed from red-brown to pale yellow. An ice-cold solution (4 ml, 0.00012 mole) of $NaB(C_6H_5)_4$ was then added at various times (Figure 1) to identical reaction mixtures. An immediate yellow precipitate was formed which was rapidly collected in a suction filter. It was washed with a 50:50 water–methanol mixture and sucked until dry (15 min). Its ir spectrum in a Nujol mull was then determined.

The product obtained after a reaction time of 90 sec was entirely the aquonitrogen salt. It was collected on a suction filter, washed with water, and dried. It was stored in a desiccator in a refrigerator.

Anal. Calcd for $[Ru(en)_2H_2ON_2][B(C_6H_5)_4]_2$: C, 68.9; H, 6.5; N, 9.3. Found: C, 68.0; H, 6.6; N, 9.1. The molar conductivity at 25° of a 10^{-3} *M* solution of the salt in dry dimethyl sulfoxide was 35 ohm^{-1} cm^2 $mole^{-1}$, which is consistent with the 2:1 electrolyte formulation. The product was diamagnetic confirming the absence of any Ru(III). Its ir spectrum showed a single strong band in the N–N stretch region at 2130 cm^{-1} and also supported the presence of coordinated water (bands at 1610 and 3500 cm^{-1}). In addition its uv spectrum had a sharp band at 220 mμ ($\epsilon \sim 13{,}000$). This corresponds with the band at 221 mμ (ϵ 16,000) reported[5] for $[Ru(NH_3)_5N_2]^{2+}$.

The starting compound, *cis*-$[Ru(en)_2N_2N_3]PF_6$, for this investigation was prepared by reaction scheme 2. The

$$\begin{tikzcd}
cis\text{-}[Ru(en)_2Cl_2]^+ \arrow[r, "Ag^+", "H_2O"'] & cis\text{-}[Ru(en)_2(H_2O)_2]^{3+} \arrow[d, "PF_6^-"', "N_3^-"] \\
cis\text{-}[Ru(en)_2N_2N_3]PF_6 & cis\text{-}[Ru(en)_2(N_3)_2]PF_6 \arrow[l, "65^\circ", "30\ min"']
\end{tikzcd} \tag{2}$$

dichloro complex was prepared by the method described earlier.[6] The azidonitrogen complex was obtained by the solid-state decomposition of the diazido compound. These two compounds have been characterized by means of elemental analyses, evolution of N_2 by Ce(IV) oxidation, conductivity, magnetic susceptibility, ir and uv spectra, and optical activity. Details of the syntheses of these and related compounds will be published later.

Acknowledgment. We wish to thank Dr. T. Studer, who initiated our studies on metal–nitrogen complexes, for his helpful experiments and discussions. This research was supported in part by grants from the National Institutes of Health and the National Science Foundation.

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(4) D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).

(5) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *ibid.*, **89**, 5595 (1967).

(6) J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc., A*, 546 (1967).

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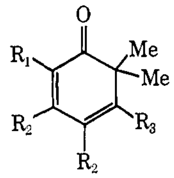
A New General Photochemical Reaction of 2,4-Cyclohexadienones

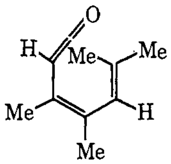
Sir:

Recently we showed that hexamethyl-2,4-cyclohexadienone forms a ketene efficiently from an unspecified singlet excited state.[1] We now have evidence that this well-known photochemical reaction of 2,4-cyclohexadienones[2] arises from the dienone n,π* singlet state. In addition we wish to describe a method for reversing the energies of the n,π* and π,π* states and a new general type of isomerization of these compounds which occurs from the first π,π* singlet state of the dienone.

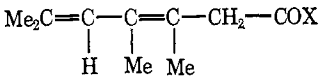
The uv spectrum of dienone **1a**[3] shows well-separated π,π* and n,π* bands at 302 and 354 mμ, respectively, in hexane. The latter was characterized by its low extinction coefficient (ϵ 130), blue shift in polar solvents, and vibrational spacing of approximately 1200 cm^{-1}.[4] Selective excitation of the n,π* band resulted in the efficient formation of ketene **2**, which was detected by ir at −100° (ν_{max} 2100 cm^{-1}), and was readily trapped as the amide **3a** with dimethylamine or the ester **3b**[3] with ethanol. The combined results from the hexamethyldienone and dienone **1a** suggest that the photochemical cleavage of the 1,6 bond in 2,4-cyclohexadienones can occur efficiently (but not necessarily exclusively) from the n,π* singlet state.



1a, $R_1 = R_3 = H; R_2 = Me$
b, $R_1 = Me; R_2 = R_3 = H$
c, $R_1 = H; R_2 = R_3 = Me$
d, $R_1 = R_2 = R_3 = H$



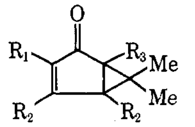
2



$$Me_2C{=}\underset{H}{C}{-}\underset{Me}{C}{=}\underset{Me}{C}{-}CH_2{-}COX$$

3a, $X = NMe_2$
b, $X = OEt$

Although dienone **1a** is photochemically inert in nonnucleophilic solvents,[3] we have observed that in trifluoroethanol it was smoothly converted to a product which did not arise by trapping of the ketene **2** by the solvent. The product was identified as the isomeric bicyclic ketone **4a** on the basis of its elemental analysis, infrared ($\nu_{C=O}$ 1692 cm^{-1}), nmr (τ 8.51 (1 H, s), 8.59 (3 H, s), 8.76 (3 H, s), 8.86 (3 H, s), 4.55 (1 H, q, *J* =



4a, $R_1 = R_3 = H; R_2 = Me$
b, $R_1 = Me; R_2 = R_3 = H$
c, $R_1 = H; R_2 = R_3 = Me$

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(1) J. Griffiths and H. Hart, *J. Am. Chem. Soc.*, **90**, 3297 (1968).

(2) (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960). (b) For a review see G. Quinkert, *Angew. Chem. Intern. Ed. Engl.*, **4**, 211 (1965).

(3) H. Hart and R. M. Lange, *J. Org. Chem.*, **31**, 3776 (1966).

(4) J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).