Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

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(5) Satisfactory elemental analyses and spectral data have been obtained on all new compounds.

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(19) National Science Foundation Fellow, 1976–1979.

(20) Address to which correspondence concerning the study should be sent.

Paul G. Gassman,* Joseph J. Valcho, Gary S. Proehl[19]

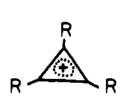
Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455[20]*, and*
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received August 15, 1978

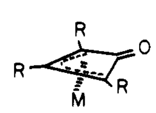
Interactions of Small Organic Rings with Transition Metals. Formation of η^3-Cyclobutenonyl Complexes by the Ring Expansion of 2-Cyclopropene-1-carbonyl Metal Species

Sir:

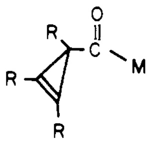
Reactions of cyclopropenium cations with transition metal complexes have been only moderately successful in the preparation of η^3-cyclopropenyl metal complexes.[1] Typical alternative reaction pathways have been shown to afford complexes derived from direct insertion of the metal into the three-membered ring,[2] or, in a more unusual reaction, the formation of four-membered-ring cyclobutenonyl complexes by a ring expansion with incorporation of carbon monoxide.[3] Thus, cations **1a–c** have been shown to afford the complexes **2a–d** on reaction with the appropriate metal carbonyl anion.[3] It has been suggested that the mechanism of this ring-expansion reaction involves attack on coordinated CO to afford an intermediate, coordinatively unsaturated, cyclopropenyl carbonyl metal species of general structure **3**, which then undergoes ring expansion.[3d,4] We here present direct evidence for such a mechanism and describe unusual spectroscopic and chemical properties of the cyclobutenonyl ligand.



1a. R = Ph.
1b. R = Me.
1c. R = ᵗBu.



2a. M = Co(CO)$_3$; R = Ph.
2b. M = Fe(CO)$_2$(NO); R = Ph.
2c. M = Co(CO)$_3$; R = Me.
2d. M = Fe(C$_5$H$_5$)(CO), R = ^{t}Bu.



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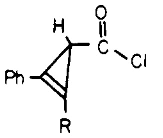
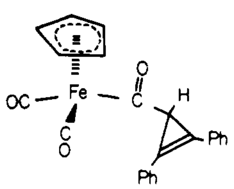


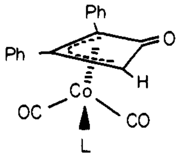
4a. R = Ph.
4b. R = *p*-MeOC$_6$H$_4$
4c. R = Me.



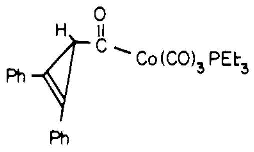
5.

Reaction of equimolar amounts of the 2-cyclopropene-1-carbonyl chloride **4a**[5] and Fe (η^5-C_5H_5)(CO)$_2^-$Na$^+$ [6] in tetrahydrofuran (THF) afforded, after dry column chromatography, the coordinatively saturated 2-cyclopropenyl-1-carbonyl-iron complex **5**, in which the cyclopropene ring remains intact.[7] Complex **5** can be recovered unchanged from refluxing hexane; ultraviolet irradiation of **5** in hexane led to decomposition, affording [Fe(η^5-C_5H_5)(CO)$_2$]$_2$ as the only metal-containing product. No ring expansion to form a product analogous to **2d**[3d] was observed.

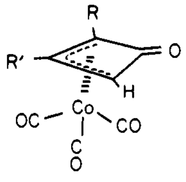
In contrast, reaction of **4a** with Co(CO)$_3$L$^-$Na$^+$ (L = CO, PPh$_3$, PPh$_2$Me, PMe$_2$Ph, PEt$_3$) in THF afforded the cyclobutenonyl complexes **6a–e** in excellent yields.[8] Complexes **6b–e** could also be prepared in essentially quantitative yield by reaction of **6a** with equimolar amounts of the appropriate tertiary phosphine (C_6H_6, 25 °C). Infrared monitoring of the reaction of Co(CO)$_3$(PEt$_3$)$^-$Na$^+$ with **4a** exhibited transient absorbances at 2075 (m), 2041 (s), 2017 (s), and 1651 (m) cm^{-1}, characteristic[9] of an acyl species **7**. These bands were rapidly



6a. L = CO.
6b. L = PPh$_3$
6c. L = PPh$_2$Me.
6d. L = PPhMe$_2$.
6e. L = PEt$_3$.



7.



8a. R = Ph; R' = *p*-MeOC$_6$H$_4$
8b. R = *p*-MeOC$_6$H$_4$; R = Ph.
8c. R = Ph; R' = Me.
8d. R = Me; R' = Ph.

replaced by the absorbances at 2023 (s), 1977 (s), and 1691 (m) cm^{-1}, of the final product **6e**. We have been unable to isolate the intermediate **7** in pure form.

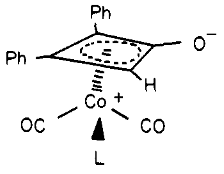
Adjustment of the steric and electronic demands of the ring substituents resulted in little selectivity regarding the site of carbon-carbon bond cleavage in the three-membered ring. Acid chloride **4b**[10] afforded a 1.0:1.0 mixture[11] of **8a** and **8b** on reaction with $Co(CO)_4^-$, whereas the aryl-alkyl-disubstituted acid chloride **4c**[12] yielded a 1.0:1.4 mixture of **8c** and **8d**.[13]

These observations can only be reconciled in terms of the originally proposed mechanism for the formation of the cyclobutenonyl-cobalt system;[3d] the acyl species of general structure **3** is indeed the first-formed complex intermediate which rearranges to the cyclobutenonyl ligand. In contrast to the observed inertness of the iron complex **5** toward thermal loss of a terminal CO ligand, such CO dissociation from a cobalt complex such as **7** is expected, and is observed, to be relatively facile.[6] The stability of **5** and the lability of **7** toward ligand dissociation clearly define the generation of a vacant coordination site on the metal as a prerequisite for ring expansion; interaction of the metal with the ring must therefore be a key step. Two such modes of interaction are possible, with the σ framework of the ring or with the olefinic function. The latter seems probable in view of the observed thermal stabilities of saturated cyclopropylcarbonyl-metal complexes.[14] The preference for cleavage of the cyclopropene ring adjacent to the methyl group in the ring expansion reaction of **4c** presumably reflects a steric effect; electronic effects involving charge buildup on either olefinic carbon atom should have manifested themselves in the reaction of **4b**,[15] in which no preference was observed.

It is noteworthy that this synthetic route provides a much higher yield route into the η^3-cyclobutenonyl-cobalt system than those previously described.[3a,b,d] The ring-expansion reaction appears to be unique to transition metal substituted cyclopropene systems; ring expansion reactions of other 2-cyclopropenyl-1-carbonyl moieties which involve initial nucleophilic attack at the carbonyl function afford five-membered-ring furan skeletons.[16] The precise nature of the ring-expansion reaction is still unclear, although a metal-promoted 1,2-migration reaction appears attractive.[4]

The infrared spectra of the cyclobutenonyl complexes **6** are of particular interest; the stretching frequency of the ring ketone ($\nu_{C=O}$) is markedly dependent upon the nature of L in the $Co(CO)_2L$ fragment (Table I). An increase in the donor ability of L is accompanied by a pronounced shift to low frequency of $\nu_{C=O}$.

The bonding in the cyclobutenonyl-metal system may be described in terms of two canonical forms, one which we have already depicted as the η^3 form **6**, and the zwitterionic **9** comprising an η^4-coordinated anion of the unknown hydroxycyclobutadiene. Increased contribution from **9** as the donor ability of L is increased is expected, and explains the observed trend in $\nu_{C=O}$. The chemistry of these cyclobutenonyl complexes also reflects this feature.



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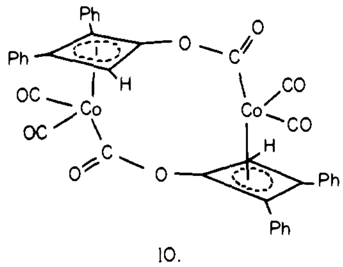

10.

Table I

complex	$\nu_{C=O}$ (ring)	L
6a	1734	CO
6b	1707	PPh_3
6c	1699	PPh_2Me
6d	1692	$PPhMe_2$
6e	1691	PEt_3

Complex **6a** exists in benzene solution in equilibrium with the novel complex **10**. At ambient temperature this equilibrium, as evidenced by infrared spectroscopy, lies essentially quantitatively on the side of **6a**. In refluxing benzene, however, the infrared spectrum of the solution exhibits almost quantitative conversion to **10** (ν_{CO} 2041 (s), 1998 (s), 1626 (m) cm^{-1}). Cooling to ambient temperatures quickly reestablishes the spectrum of **6a**. Analogous reflux of **6a** in hexane solution results in precipitation of the less soluble **10** as a brown, amorphous solid. Dissolution of **10** in benzene or dichloromethane at room temperature rapidly regenerates **6a**. Formation of **10** can be viewed as resulting from nucleophilic attack of the negatively charged ligand oxygen in **9** on carbon monoxide complexed to a cationic metal center. Such reactions are well documented. The nucleophilicity of the ligand oxygen atom in complexes **6** has also been used to generate a range of neutral and cationic η^4-cyclobutadiene complexes of cobalt(I).[17] Further studies of the chemistry of the cyclobutenonyl and related ligand systems are in progress.

Acknowledgment. We gratefully acknowledge the support of the Research Corporation and the National Science Foundation (Grant CHE 77-17877).

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(6) R. B. King, *Acc. Chem. Res.*, **3**, 417 (1970).

(7) Yield 70%; ν_{CO} (hexane) 2016 (s), 1960 (s), 1638 (m) cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 4.76 (s, C_5H_5), 3.45 (s, CH), 7.2–7.8 (m, Ph); ^{13}C NMR (15 MHz, $CDCl_3$) 262.8 (C=O), 214.7 (C≡O), 112.4 (Ph*C*⩽), 86.4 (C_5H_5), 47.6 (CH); mass spectrum *m/e* 396 (P^+).

(8) (a) Complex **6a:** ν_{CO} (hexane) 2088 (s), 2038 (s), 2027 (s), 1734 (m) cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.09 (s, CH), 7.3–7.9 (m, Ph); mass spectrum *m/e* 362 (P^+). (b) Complex **6d:** ν_{CO} (hexane) 2029 (s), 1980 (s), 1692 (m) cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 4.42 (d, J = 2.8 Hz, CH), 7.1–7.8 (m, Ph), 1.51 (d, J = 8.3 Hz, *P*-Me), 1.61 (d, J = 8.4 Hz, *P*-Me); mass spectrum *m/e* 472 (P^+). (c) Satisfactory infrared, ^{1}H NMR, ^{13}C NMR, and mass spectra were obtained for all other complexes **6**. Satisfactory microanalyses were obtained for all compounds reported here.

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(10) (a) Prepared from the corresponding acid[10b] by the method of ref 5. (b) R. Breslow, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

(11) The resonances in the ^{1}H NMR spectrum of the mixture corresponding to the ring protons in **8a** and **8b** (δ 5.04 (s), 5.08 (s)) were of equal area within the limits of integration.

(12) (a) Prepared from the corresponding acid[12b] by the method of ref 5. (b) A. B. Thigpen and R. Fuchs, *J. Org. Chem.*, **34**, 505 (1969).

(13) Resonances in the ^{1}H NMR spectrum of the crude mixture of **8c** and **8d** were

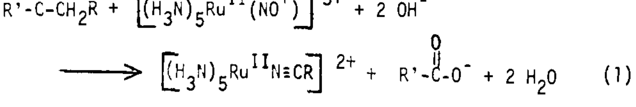
assigned by comparison with the reported spectrum of **2c**[3b] in which the assignments of methyl resonances are unambiguous by integration. Thus, the mixture of **8c** and **8d** exhibited two methyl resonances at δ 2.41 (s) (relative intensity 1.0) and at δ 2.09 (s) (relative intensity 1.4). The higher field, higher intensity, methyl resonance must be that in the isomer with the methyl group in the terminal position of the η^3-allyl portion of the cyclobutenonyl ligand, i.e., **8d**. The corresponding ring proton resonances are δ 4.84 (s) (**8c**) and δ 5.15 (s) (**8d**).
(14) M. I. Bruce, M. Z. Iqbal, and F. G. A. Stone, *J. Organomet. Chem.*, **20**, 161 (1969).
(15) R. Breslow, J. Lockhart, and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962).
(16) R. Breslow, R. Boikess, and M. Battiste, *Tetrahedron Lett.*, 42 (1960).
(17) C. E. Chidsey, W. A. Donaldson, and R. P. Hughes, manuscript in preparation.

Christopher E. Chidsey, William A. Donaldson
Russell P. Hughes,* Paul F. Sherwin
Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755
Received August 13, 1978

Reaction of Nitrosylpentaammineruthenium(II) Ion with Organic Carbonyls Containing an α-Methylene Group: Facile Oxidative Cleavage of a Carbon-Carbon Bond

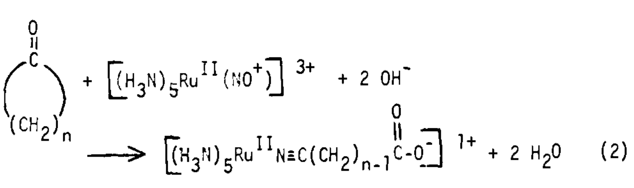
Sir:

We report the facile oxidative cleavage of ketones (and aldehydes) by the action of nitrosylpentaammineruthenium(II) ion in dilute aqueous base. The stoichiometries shown in eq 1 and 2 have been established for open chain compounds (**1**) and for cyclic ketones (**2**).



$$R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2R + [(H_3N)_5Ru^{II}(NO^+)]^{3+} + 2\,OH^- \longrightarrow [(H_3N)_5Ru^{II}N{\equiv}CR]^{2+} + R'\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^- + 2\,H_2O \tag{1}$$

where R = alkyl or phenyl and R' = H, alkyl, or phenyl



where n = 4, 5 or 6.

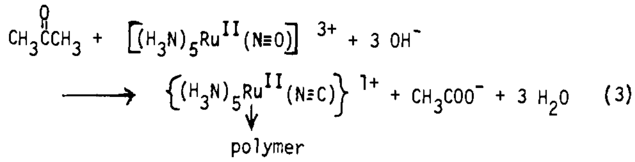
The only ruthenium-containing products are nitrilepentaammineruthenium(II) species, which are isolated as perchlorate salts and identified by comparing infrared and electronic spectra with those in the literature.[1,2] Table I lists some typical carbonyl compounds which have been used, the nitrile products, and their yields. In those cases in which the organic compound dissolves completely in 0.1 M NaOH, the reaction appears to be complete within 10 min at room temperature. The benzoate ion has been identified as a major reaction product in the reaction with $C_6H_5CH_2C(O)C_6H_5$ as substrate by conversion to benzoic acid and identification via infrared, NMR, and melting point. The products from the reactions with cyclic ketones exhibit, as expected, infrared peaks distinctive for both nitrile and carboxylic acid functions.

A reaction also occurs with compounds containing α-methyl but no other α-hydrogen atoms (e.g., acetone and acetaldehyde). These reactions produce intractable products as would be expected from the known chemical behavior of the cyanopentaammineruthenium(II) ion.[3] Reaction 3 thus provides on alternative to the haloform reaction.

Table I. Typical Results with Compounds Containing α-Methylene Groups

carbonyl	nitrile product $(H_3N)_5RuN{\equiv}CR^{2+}$, R	% yield[a]
CH_3CH_2CHO, propanal	CH_3	67
$CH_3CH_2C(O)CH_2CH_2$, 2-pentanone	CH_3	55
$CH_3CH_2C(O)CH_3$, 2-butanone	CH_3	79
$C_6H_5CH_2CHO$,[b] phenylacetaldehyde	C_6H_5	49
$C_6H_5CH_2C(O)C_6H_5$,[b] benzyl phenyl ketone	C_6H_5	44
$CH_2{=}CHCH_2CH_2C(O)CH_3$,[b] 5-hexen-2-one	$CH_3CH{=}CH$[c]	23
$\overline{CH_2(CH_2)_5C}{=}O$,[b] cycloheptanone	HOOC-$(CH_2)_4CH_2$[d]	87

[a] Based on weight of recrystallized perchlorate salts. [b] Limited solubility in 0.1 M NaOH. [c] Note that the double bond undergoes *base-catalyzed* isomerization into a conjugated position. [d] Acidified before perchlorate addition.



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 + [(H_3N)_5Ru^{II}(N{\equiv}O)]^{3+} + 3\,OH^- \longrightarrow \{(H_3N)_5\underset{\substack{\downarrow\\ \text{polymer}}}{Ru^{II}}(N{\equiv}C)\}^{1+} + CH_3COO^- + 3\,H_2O \tag{3}$$

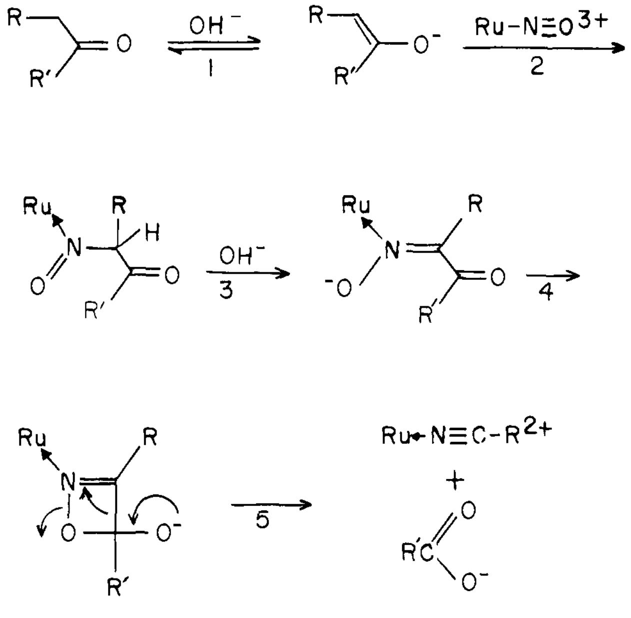
When *both* methyl and methylene groups are present (e.g., 2-butanone) the reaction occurs predominantly at the methylene carbon. Decreasing the pH to 7 stops the reaction as does increasing OH^- to 2 M (which is known to convert the nitrosyl ligand to nitrite[4]).

Most of the previously reported reactions of the $Ru^{II}NO^{3+}$ moiety have involved nitrogen containing species such as hydrazine,[5] hydroxylamine,[5] azide,[6] aromatic[7] and aliphatic[8] amines, and coordinated amido ligands[8,9] to form new nitrogen-nitrogen bonds, although formation of N-coordinated nitroso[10,11] and oxime[12,13] complexes have also recently been noted.[14] This report represents the first case in which a carbon-nitrogen triple bond is formed and in which a carbon-carbon bond is cleaved by the reaction of $Ru^{II}NO^{3+}$ or any other metal nitrosyl species.

The mechanism in Scheme I is postulated.[15]

The driving forces for the above reaction are the formation of a CO_2^- chromophore, the high electrophilicity of the NO^+ ligand,[16] and the well-established stabilization of Ru(II) complexes by π-acceptor ligands such as nitriles via dπ-pπ* back-bonding.[17]

Scheme I



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