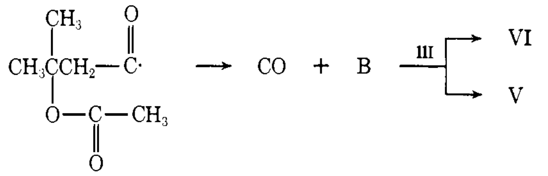
Table I. Products from the Benzoyl Peroxide Initiated Decarbonylation of III at 75°

Reaction	$[\mathrm{III}]^0$ × 10^2 *M*	Solvent	Concn × 10^2 $M^{a,b}$ of products					VI:V
			C_4H_7CHO	CH_3CO_2H	V	VI	III^f	
1	270.0	C_6H_6	44	6	26	2.5	108	0.09
2	94.06	C_6H_6	15	4.7	17	2.9	52	0.17
3	71.31	C_6H_6	14	4.4	13	2.7	33	0.20
4	50.38	C_6H_6	6.2	2.0	5.2	1.4	31	0.27
5	50.20	C_6H_5Cl		4.2	5.3	1.3	22	0.25
6	19.11	C_6H_6	4.4	1.0	1.5	0.6	4.4	0.43
7	18.80	C_6H_5Cl		2.0	1.4	0.8	11	0.57
8	10.76	C_6H_6	3.3		0.7	0.5	1.8	0.71
9	10.69	C_6H_5Cl			0.5	0.4	6.5	0.80

[a] Products V and VI were quantitatively analyzed on a 5% 1/8 in. × 13 ft SF-96 glpc column. The remaining products were quantitated using a 5% 1/8 in. × 13 ft Ucon Polar glpc column. The response of all products to the flame ionization detector was calibrated with an added standard, bromobenzene. [b] The symbols $[\mathrm{III}]^0$ and $[\mathrm{III}]^f$ refer to the initial and final concentration of aldehyde III after the reaction had been carried out for 72 hr.

In principle it is possible to distinguish between these two mechanistic possibilities since the relative rates of formation of the two products VI and V would be independent of aldehyde concentration if a common intermediate, B, were involved in their respective formations.


(4)

When benzene or chlorobenzene solutions containing varying concentrations of II (2.7–0.1 *M*) were heated (75°) with benzoyl peroxide (10 mol %) in sealed degassed Pyrex ampoules, for 72 hr, it was found that, aside from carbon monoxide, acetic acid, β-methylcrotonaldehyde, and unreacted starting material, only compounds VI and V where formed (see Table I). A material balance accounted for up to 93% of the starting aldehyde. Both the rearranged (VI) and the unrearranged (V) acetates were shown to be stable under the reaction conditions, while the starting aldehyde slowly yielded β-methylcrotonaldehyde by a concomitant thermal elimination. When isobutylene was added to the reaction mixture prior to reaction, it could be quantitatively reisolated at the conclusion of the reaction. Furthermore (see Table I), as the concentration of III was increased the ratio of V:VI increased uniformly.

The rapid rate of acetoxy radical decarboxylation,[11,12] the absence of isobutylene as a reaction product, and the lack of reaction of added isobutylene make an elimination–readdition process an unattractive mechanism for the observed rearrangement although this type of pathway, as a cage process, cannot be ruled out.[13–15]

The concentration dependence of the ratio of V:VI clearly demonstrated the absence of a common intermediate in the formation of both products and necessitates that structure B serves as a transition state, or an unreactive intermediate, on the path to the formation of the rearranged radical, C, the driving force for the reaction being the transformation of a primary radical into a more stable tertiary radical. Alternatively, structure B plus one of the other intermediate radicals (A or C) can function as the precursers for the formation of V and VI. Since bis(α-alkoxyalkyl) radicals have been proposed as stable species,[16] the involvement of B as an intermediate must be considered.

Under conditions identical with the ones necessary to produce rearranged acetate from the decarbonylation of III, the decarbonylation of IV yields only isopropyl acetate (VII), and it appears that the stability gained by the rearrangement of an acetoxy group from a secondary to a primary position is insufficient to overcome the activation energy necessary for its migration.

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(11) M. Szwarc, "Peroxide Reaction Mechanisms," John Wiley & Sons, Inc., New York, N. Y., 1960, p 173.

(12) W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

(13) J. C. Martin, J. W. Taylor, and E. H. Drew, *J. Am. Chem. Soc.*, **89**, 129 (1967).

(14) H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963).

(15) H. J. Shine and J. R. Slagle, *ibid.*, **81**, 6309 (1959).

(16) E. S. Huyser, R. Kellogg, and D. T. Wang, *J. Org. Chem.* **30**, 4377 (1965), and references cited therein.

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A Novel Nitrosyl-Substituted Metal Carbonyl Cluster

Sir:

Metal nitrosyls and metal carbonyl clusters both are attractive potential homogeneous catalysts. The nitrosyls are frequently more reactive than isoelectronic carbonyls, and this tendency has been exploited in catalytic applications.[1,2] Clusters offer the possibility of catalysis involving more than one metal center, similar to the mechanism proposed recently by Schrauzer[3] for the catalysis of the dimerization of bicyclo[2.2.1]-heptadiene-2,5 by $Zn(Co(CO)_4)_2$. Unfortunately, clusters sufficiently robust to survive typical conditions for catalytic processes have in our experience often proved unreactive. In view of the apparent activating effect of coordinated nitrosyl, a reasonable synthetic objective is then the preparation of nitrosyl carbonyl clusters.

The well-known affinity of ruthenium for nitrosyl ligands suggested an investigation of the reaction of

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(1) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, **91**, 5659 (1969).

(2) J. P. Candlin and W. H. Janes, *J. Chem. Soc., C*, 1856 (1968).

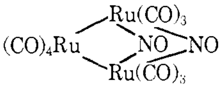
(3) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Amer. Chem. Soc.*, **88**, 4890 (1966).

$Ru_3(CO)_{12}$ with nitric oxide. In an early paper, Manchot[4] had reported several products from the reaction of solid $Ru_3(CO)_{12}$ with NO, including one formulated as $Ru(NO)_5$.[5] Candlin[6] later reported that reaction of "moist NO" with $Ru_3(CO)_{12}$ in boiling CH_2Cl_2 gave a brown polymer whose elemental analyses were consistent with the formula $[Ru(CO)_2(NO_2)_2]_x$ and which had infrared absorption maxima at 2120, 2090, 2050, 1910, 1270, 1170, and 840 cm^{-1}. Our hope was that conditions could be found under which the cluster $Ru_4(CO)_8(NO)_4$, isoelectronic with $Rh_4(CO)_{12}$, would be formed.

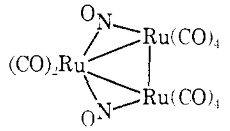
In preliminary experiments we found that the products of reaction between $Ru_3(CO)_{12}$ and NO depended strongly upon the purity of the nitric oxide. For example, nitrogen dioxide, which is present in commercial NO and which is rapidly generated by reaction of NO with air, reacted almost instantaneously with $Ru_3(CO)_{12}$ in benzene at 25° giving an insoluble yellow substance of approximate empirical composition $[Ru(CO)_3(NO_2)]_x$ (*Anal.* Calcd for RuC_3NO_5: C, 15.59; N, 6.06; H, 0.0. Found: C, 16.08; N, 6.08; H, 0.3), having infrared absorption bands (KBr pellet) at 2122 (s), 2050 (vs, broad), 2005 (m), 1490 (m, broad), 1380 (vs), 1320 (m), 1270 (m), 1180 (w, broad), 830 (m), and 814 (m) cm^{-1}. Many of these bands are present in the spectrum of Candlin's brown polymer.[6] Nitric oxide freed from NO_2 and H_2O by successive passage through 4 *N* NaOH and silica gel did not react with $Ru_3(CO)_{12}$ in benzene at 25° or in boiling CH_2Cl_2. In boiling benzene, however, passage of NO through the solution for a few minutes led to deposition of an insoluble brown polymer and the production of greenish brown solution. These solutions were flushed with N_2, cooled to 25°, filtered, and then concentrated under vacuum. Addition of *n*-hexane led to slow formation of dark green needles of the new nitrosyl carbonyl cluster $Ru_3(CO)_{10}(NO)_2$, obtained in 30–40% yield. *Anal.* Calcd for $Ru_3C_{10}N_2O_{12}$: C, 18.67; N, 4.35; H, 0.0; mol wt, 643. Found: C, 18.87; N, 4.26; H, 0.0. Replacement of benzene by cyclohexane gave similar results, but only a very slow reaction was observed in boiling chloroform, and in boiling *n*-heptane the brown polymer was the principal product. In the last case, the brown polymer contained about a 1:1 ratio of carbon to nitrogen. Under similar conditions the trisubstituted complex $Ru_3(CO)_9(PPh_3)_3$ was relatively unreactive toward NO.

The formulation of the green cluster as $Ru_3(CO)_{10}(NO)_2$ has been confirmed by low-resolution mass spectroscopy. A parent ion multiplet centered at mass 643 has been observed, along with twelve other multiplets corresponding to the loss of twelve ligands to give Ru_3^+.[7] The complex contains two more electrons than $Ru_3(CO)_{12}$ and cannot be regarded as a simple substitution product of that cluster.

The infrared spectrum of $Ru_3(CO)_{10}(NO)_2$ in cyclohexane has ν_{CO} 2110 (w), 2077 (s), 2068 (s), 2061 (sh), 2038 (s), 2030 (s), 2026 (sh), 2015 (w), and 2000 (m) cm^{-1} and ν_{NO} 1524 (w) and 1508 (m) cm^{-1}. The large number of carbonyl bands implies a low molecular symmetry, while the low ν_{NO} suggests[8] that the nitrosyls are bridging. The proposed structures **1a** and **1b** are both consistent with the analysis and spectroscopic data.



1a



1b

Complex **1** is indicated by magnetic susceptibility measurements to be diamagnetic. It is moderately air stable and slightly soluble in most organic solvents. It is unstable above 70° in solution under N_2, giving dark brown decomposition products. Two catalytic reactions of **1** have been investigated. Complex **1** reacts with dimethylacetylenedicarboxylate and the trimer hexakis(carbomethoxy)benzene was detected by vpc analysis. Stirring of a solution of 5 mg (8 μmoles) of **1** and 0.50 ml (0.34 g; 3950 μmoles) of 1-hexene in 3 ml of benzene for 22 hr under 56 psi of hydrogen led to extensive isomerization of the hexene and a small amount of hydrogenation to *n*-hexane. Although evaporation of the solvent under vacuum produced the cluster **1** unchanged, a parallel experiment without hydrogen produced no isomerization.

Other catalytic reactions of **1** and the results of an X-ray crystallographic study and of attempts to prepare other nitrosyl-substituted metal carbonyl clusters will be reported at a later time.

(4) W. Manchot and W. J. Manchot, *Z. Anorg. Allg. Chem.*, **226**, 385 (1936).

(5) Manchot's analytical data actually agree somewhat better with the formulation $Ru(NO)_2(NO_2)_2$ which is probably more reasonable.

(6) J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. Ind.* (London), 1960 (1966).

(7) The multiplets are due to the complex isotopic distribution of the triruthenium unit. Computer analysis of the entire spectrum is in progress.

(8) For example, in di-μ-nitrosyl-bis(nitrosyl-π-cyclopentadienylchromium) the terminal nitrosyl frequency is 1672 cm^{-1} while that of the bridging nitrosyls is 1505 cm^{-1}; *cf.* R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964), and R. B. King, *ibid.*, **6**, 30 (1967), for this and other examples.

(9) National Science Foundation Predoctoral Fellow 1967–present.

(10) On leave from Princeton University Feb–Aug 1969.

(11) (a) Author to whom inquiries should be addressed. (b) This work was supported by National Science Foundation Grant No. GP 9101 and the Advanced Research Projects Agency through the Center for Materials Research at Stanford University.

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Pulse Radiolysis of Aqueous Solutions of Cobalt Cyanide Complexes. The Detection of Pentacyanocobaltate(I) and Other Transients

Sir:

We report here some results of pulse radiolysis experiments on aqueous solutions of cobalt cyanide complexes, including the direct detection of several important transient species, among them pentacyanocobaltate(I). Although the latter species has been postulated as a reaction intermediate[1,2] and has been the subject of considerable interest and speculation, it does not appear to have previously been directly observed.

Hydrated electrons (e_{aq}^-) were generated in deaerated solutions containing various cobalt cyanide complexes, using 0.4-μsec pulses of 15-MeV electrons from Ar-

(1) J. Hanzlik and A. A. Vlček, *Inorg. Chem.*, **8**, 669 (1969).

(2) J. Hanzlik and A. A. Vlček, *Chem. Commun.*, 47 (1969).