of the axial sites. The pyridine rings would be restricted in their thermal motion and provide a more effective shielding of the sixth coordination site. This restriction would make the *trans* site on the adjacent copper ion available for coordination. This model is consistent with the reaction of the 1:1 complexes with coordinating ligands, such as water or dimethyl sulfoxide, and with the existence of the 2:1 dimeric pyridine N-oxide complex, $[(C_5H_5NO)_2CuCl_2]_2$.[5]

The *o*-hydrogen atoms on the pyridine ring do not provide maximum shielding of the sixth coordination site in the solid, but the hydrogen H(3) on one chain occupies this site on an adjacent chain. The Cu–H(3) separation is 2.8 Å, and although the distance is too long to be considered a normal bond, the electrostatic interaction should affect the electron distribution around the copper ion.

The low magnetic moment of $[(C_5H_5NO)CuCl_2]_2$ is attributed to a superexchange mechanism. This is qualitatively described as a direct transfer *via* overlap of the odd-electron Cu(II) orbitals which have been expanded by a mixture with oxygen orbitals of appropriate symmetry. The magnetic electrons probably occupy orbitals of approximately $d_{x^2-y^2}$ symmetry, and the exchange interaction predominantly occurs through basal ligands of the pyramidal geometry. Attempts to correlate the exchange energy with substituents on the pyridine ring have not been too successful, and this may be due to intermolecular perturbations, such as the Cu–H(3) interaction, which affects the electron distribution.

The 2:1 dimeric complex $[(C_5H_5NO)_2Cu(NO_3)_2]_2$[6] also is an oxygen-bridged dimer with the geometry around the Cu(II) ions closely approximating a square-based pyramid; however, the magnetic moment is normal. Each bridging oxygen atom in this complex is at the apex of one of the pyramids, and the magnetic electron orbitals do not overlap significantly. The oxygen bridging in this complex may be rationalized in terms of the steric effect of the nitrate ligands rather than an electronic effect.

The two infrared bands in $[(C_5H_5NO)CuCl_2]_2$ assigned to Cu–Cl stretching vibrations[7] now can be understood. The band at 330 $cm^{-1}$ is consistent with a nonbridged chloride ion, and the band at 311 $cm^{-1}$, with the weakly bridged chloride ion. The variation in solubilities and infared band positions for the 1:1 complexes can be related to the strength of the Cu–Cl bridging interaction. The complexes probably exist as dimers in solution, as indicated by molecular weight measurements.[8]

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## The Kinetics of Nitrosyl Exchange in Some Metal Nitrosyls in the Gas Phase

By Frank A. Palocsay and John V. Rund

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Carbonyl-exchange and -substitution reactions of metal carbonyls have been widely studied. The rates are first order in the metal compound and zero order in the attacking ligand for most simple metal carbonyls and related organometallics.[1,2] Some cyclopentadienylmetal carbonyls[3] and square-planar complexes of heavier transition metals[4] (*e.g.*, $Rh_2(CO)_4Cl_2$) exchange carbonyls by a second-order mechanism, presumably owing to the ease with which they form intermediates of higher coordination numbers.

The nitrosyl carbonyls that have been studied, $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$,[5] give different results. Carbonyl exchange is significantly slower than that of the isoelectronic $Ni(CO)_4$. NO is a three-electron donor that is supposed to increase the electron density on the metal more than CO does. This increase strengthens the M–C bonding and decreases the rate of carbonyl exchange. The conclusion is supported by the carbonyl stretching frequencies of the compounds.[6] Substitution of a carbonyl by a phosphine or an amine is a second-order process.[7] The great polarizability of the nitrosyl group may allow it to accept electron density from the metal upon the approach of a nucleophile and so increase the ease with which an intermediate of higher coordination number is formed. That no substitution of the nitrosyl group has been observed during these reactions is not unexpected, for the M–N bond is stronger than the M–C bond and also the compound formed by direct substitution would be reactive because it does not obey the "rule of eighteen." Little work has been done on the kinetics and mechanism of nitrosyl-exchange or -substitution reactions, not even on establishing that such reactions occur. We report a study of the nitrosyl-exchange reactions of $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$, and $(C_5H_5)NiNO$ in the gas phase.

### Experimental Section

**Chemicals.**—$Fe(CO)_2(NO)_2$,[8] $Co(CO)_3NO$,[9] and $(C_5H_5)NiNO$[10]

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were prepared by published methods. They were characterized and checked for purity by mass spectrometry. The $^{15}$NO (95% enrichment) was purchased from Bio-Rad Laboratories.

**Kinetics.**—The reactions were run in glass bulbs of known volume. The reactants were introduced and their concentrations were determined by what was essentially a one-way stopcock (a three-way stopcock shell with a hollow plug of known volume having only one hole) on a vacuum line. Each reactant was allowed to enter the plug at a measured pressure. The stopcock was then turned so that the reactant in the plug could be condensed into the reaction vessel. The concentrations of the reactants were calculated from the pressures and volumes. The bulb was warmed to room temperature and attached to a Hitachi Perkin-Elmer RMU-6E mass spectrometer. The initial abundance ratio of metal nitrosyl-$^{14}$N to metal nitrosyl-$^{15}$N was measured. The bulbs were thermostated and protected from light. Incorporation of $^{15}$NO into the metal nitrosyl compound was measured at intervals of a few days. Samples removed by the mass spectrometer were small enough that the over-all reactant concentrations were practically unchanged.

The method of McKay[11] was used to calculate the rate constants. The apparent first-order rate constant, $k_1$, was equal to the slope of a plot of ln $[(C_0 - C_\infty)/(C_t - C_\infty)]$ *vs.* time, where $C_0$, $C_t$, and $C_\infty$ are the concentrations of metal nitrosyl-$^{15}$N initially, at time $t$, and at equilibrium. It was converted to the true second-order rate constant by the equation

$$k_2 = k_1\left(\frac{Xa^{1-\alpha}b^{1-\beta}}{Xa + b}\right)$$

where $a$ and $b$ are the concentrations of the metal nitrosyl and NO, $\alpha$ and $\beta$ are the orders in metal nitrosyl and NO, and $X$ is the number of exchangeable nitrosyls in the metal nitrosyl.

## Results

Figure 1 shows a sample kinetic plot for the exchange on the nitrosyl group in Co(CO)$_3$NO. Table I lists the rate constants. The values of the observed first-order rate constant, $k_1$, are functions of the NO concentration, whereas the values of $k_2$ are constant. Thus the rate law is

$$\text{rate} = k_2[\text{Co(CO)}_3\text{NO}][\text{NO}]$$

The enthalpy of activation is 9.7 ± 1.4 kcal/mol. Figure 1 and Table II give analogous data for the reaction of Fe(CO)$_2$(NO)$_2$. The rate law is also first order in both the iron nitrosyl and NO. The enthalpy of activation is 8.3 ± 1.2 kcal/mol. Both reactions have activation entropies of about −50 eu. Wall effects were tested by increasing the available glass surface area about fivefold by the addition of glass beads to the reaction vessels. No changes in rate were observed. The reactions were also run in atmospheres of CO. Although carbonyl exchange occurs with much greater frequency than nitrosyl exchange, it had no effect on the rate of $^{15}$NO incorporation.

TABLE I

RATE CONSTANTS OF NO EXCHANGE OF Co(CO)$_3$NO

| $10^2$[Co(CO)$_3$NO], $M$ | $10^2$[NO], $M$ | $10^8k_1$, sec$^{-1}$ | $10^6k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| | | 25° | |
| 0.72 | 0.83 | 5.2 | 4.1 ± 0.2 |
| 0.82 | 0.81 | 6.5 | |
| 0.85 | 1.14 | 8.0 | |
| | | 35° | |
| 0.43 | 0.75 | 8.7 | 7.6 ± 0.14 |
| 0.49 | 0.87 | 10.4 | |
| 0.73 | 0.75 | 11.1 | |
| 0.76 | 0.81 | 11.8 | |
| 0.73[a] | 0.41 | 8.8 | 7.6 ± 0.2 |
| 0.84[a] | 0.42 | 9.5 | |
| 0.85[b] | 0.45 | 9.8 | 8.0 ± 0.14 |
| 1.05[b] | 1.34 | 19.3 | |

[a] [CO] = 5 × $10^{-3}$ $M$. [b] Reaction vessels filled with glass beads.

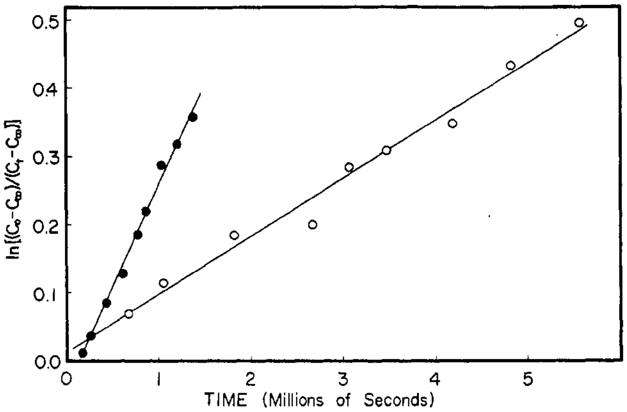

Figure 1.—Sample kinetic runs for exchange of NO in metal nitrosyls. Solid circles refer to Fe(CO)$_2$(NO)$_2$ at 25°; initial concentrations were [Fe(CO)$_2$(NO)$_2$] = 0.42 × $10^{-2}$ $M$ and [NO] = 1.08 × $10^{-2}$ $M$. Open circles refer to Co(CO)$_3$NO at 35°; initial concentrations were [Co(CO)$_3$NO] = 0.43 × $10^{-2}$ $M$ and [NO] = 0.75 × $10^{-2}$ $M$.

TABLE II

RATE CONSTANTS OF NO EXCHANGE OF Fe(CO)$_2$(NO)$_2$

| $10^2$[Fe(CO)$_2$(NO)$_2$], $M$ | $10^2$[NO], $M$ | $10^8k_1$, sec$^{-1}$ | $10^6k_2$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| | | 25° | |
| 0.41 | 0.44 | 13.7 | 18 ± 2 |
| 0.38 | 0.71 | 14.4 | |
| | | 35° | |
| 0.48 | 0.47 | 19.0 | 31 ± 2 |
| 0.76 | 0.44 | 28.2 | |
| 0.70 | 1.27 | 40.0 | |
| 1.19[a] | 1.02 | 39.1 | |
| 0.42 | 0.43 | 26.1 | |
| 0.49 | 0.72 | 35.8 | |
| 0.75 | 0.41 | 38.4 | |
| 0.63 | 0.70 | 42.3 | |
| 0.75[a] | 0.62 | 39.1 | 33 ± 1 |
| 0.70[b] | 0.43 | 34.0 | 30 ± 1 |

[a] Reaction vessels filled with glass beads. [b] [CO] = 5 × $10^{-3}$ $M$.

Nitrosyl exchange did not occur for (C$_5$H$_5$)NiNO in 30 days at 45° or in 10 days at 120°, although at the higher temperature some decomposition of the metal compound was observed.

## Discussion

The kinetics of some nitrosyl exchanges have been examined, and it is possible to make some inferences about the reaction mechanisms. A simple associative mechanism is consistent with the data

$$\text{NO}^* + \text{MNO} \longrightarrow \text{NO}^*\text{MNO} \longrightarrow \text{MNO}^* + \text{NO}$$

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M represents the metal and the nonreacting ligands. NO*MNO could be either a transition state or an intermediate of increased coordination number. The occurrence of the reaction in the gas phase rather than on the wall of the container is substantiated by the invariance of the rate with increasing surface area. A mechanism with a rate-determining dissociation of a nitrosyl group followed by rapid incorporation of a molecule of NO is inconsistent with the dependence of the rate on the concentration of NO. Furthermore, the activation enthalpies are in the usual range of associative rather than dissociative reactions.[12] The rate dependence on NO concentration could be explained by a collision between NO and metal nitrosyl that leads to a vibrationally excited state of the latter. The mechanism can be eliminated, however, because the addition of large amounts of CO does not increase the reaction rate. This observation also eliminates rate-determining dissociation of a carbonyl group followed by a rapid exchange of nitrosyls, because CO and NO would be competing for the same active intermediate, and nitrosyl exchange would be retarded by added CO. Among the possible rationalizations of $(C_5H_5)NiNO$ inertness to nitrosyl exchange are, first, that negative charge on the cyclopentadienide strengthens the Ni–N bond *via* $\pi$ bonding and, second, that the nickel compound cannot form a trigonal-bipyramidal transition state with the NO's in axial positions.

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# Amine-Catalyzed Hydrolysis of Bromomethylcarboranes

BY TAMOTSU YOSHIZAKI, MOTOO SHIRO, YUZO NAKAGAWA, AND HARUYUKI WATANABE

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Zakharkin and Kalinin[1] described the facile degradation of 1,2-dicarba-*closo*-dodecaborane(12) (*o*-carborane) with piperidine to produce an adduct of piperidine with the piperidinium salt of dodecahydrodicarba-*nido*-undecaborate(1−). It was suggested that the piperidine molecule is loosely bound to the dodecahydrodicarba-*nido*-undecaborate(1−) anion[2] by a weak dative B–N bond. However, Hawthorne, *et al.*,[3] presumptively proved the piperidine molecule to be held in the crystal lattice by hydrogen bonds and not to be bound through a B–N dative bond. The reaction of 1,2-bis(bromomethyl)-*o*-carborane with aqueous ammonia solution leads to the formation of the inner salt of C,C′-bis(aminomethyl)dodecahydrodicarba-*nido*-undecaborate(1−), which involves no B–N dative bond.[4] The present paper describes a new type of amine-catalyzed solvolysis of C-halomethyl-*o*-carboranes and the formation of trimethylamine(N–B)-7-methylundecahydro-7,8-dicarba-*nido*-undecaboron (I) and its bromo derivative (II), through it. In these molecules, the trimethylamine is bonded to a cage boron atom through a B–N dative bond.

## Experimental Section

**Trimethylamine(N–B)-B-bromo-7,8-dimethylundecahydro-7,8-dicarba-*nido*-undecaboron (II).**—In a typical run, 1.3 g of B-bromo-1-bromomethyl-2-methyl-*o*-carborane (mp 70–71.5°) prepared by the method of Smith, *et al.*,[5] was dissolved in a mixed solvent of 20 ml of methyl ethyl ketone and 4.7 ml of 30% aqueous trimethylamine. The solution was heated for 6 hr at 100° in a sealed tube, and the solvent was then removed by distillation under reduced pressure. The residue was washed with water and recrystallized from ethanol to give 0.75 g of colorless crystals, with a yield of 64% based on the composition $B_9H_{23}C_7NBr$ (II); mp 221° dec. *Anal.* Calcd for $B_9H_{23}C_7NBr$: mol wt, 298.5; C, 28.17; H, 7.77; N, 4.69; B, 32.60. Found: mol wt, 290; C, 28.16; H, 7.37; N, 4.93; B, 31.61. The molecular weight was measured in acetone with a Mechrolab Model 301A vapor pressure osmometer.

Compound II is soluble in acetone, alcohol, ether, benzene, and pyridine, but not in water.

**Trimethylamine(N–B)-7-methylundecahydro-7,8-dicarba-*nido*-undecaboron (I) and Its Isomer (III).**—On treating 1-bromomethyl-*o*-carborane in the same manner as described above, a homologous compound $B_9H_{22}C_6N$ (I), mp 152° dec, was obtained as a minor product (15% yield) along with an isomeric compound (III) (75% yield), mp 267° dec. The latter is less soluble in ethanol and is isolated from I by recrystallization from ethanol. *Anal.* I and III calcd for $B_9H_{22}C_6N$: mol wt, 205.6; C, 35.05; H, 10.78; N, 6.81; B, 47.4. Found for I: mol wt, 227; C, 35.27; H, 10.81; N, 6.76. Found for III: mol wt, 210; C, 35.22; H, 10.86; N, 6.79; B, 47.4.

**Spectra.**—Proton magnetic resonance spectra were recorded at room temperature with a Varian A-60 high-resolution nmr spectrometer at 60 Mc. Results are given in Table I. The nmr signals of protons attached to boron atoms extend over 3 ppm and are flattened to prevent their analysis.

Mass spectra were recorded on a Hitachi mass spectrometer, Model RMU-6. All spectra consist of several groups of prominent

TABLE I

PMR SPECTRA

| Compd (solvent) | $\tau$ value | Rel intens | Assignment |
|---|---|---|---|
| I | 7.020 | 9.5 | $N(CH_3)_3$ |
| (pyridine-$d_5$) | 7.330 | 1.0 (broad) | C–H |
| | 8.350 | 3.0 | $C–CH_3$ |
| II | 6.758 | 9.0 | $N(CH_3)_3$ |
| (acetone-$d_6$) | 8.425 | 6.0 (broad) | $CH_3$, $CH_3$ |
| III | 5.860 | 9.0 | $N(CH_3)_3$ |
| (pyridine-$d_5$) | 6.092, 6.300 | 2.0 (AB type) | $CH_2$ |
| | 6.535, 6.682 | | |
| | 7.6 | 0.8 (broad) | CH |

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