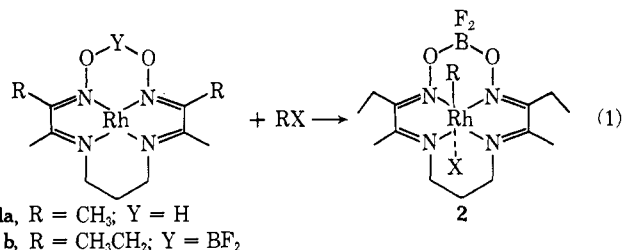


## A Neighboring Group Effect during Oxidative Addition

Sir:

Earlier we reported<sup>1</sup> a macrocyclic rhodium(I) complex, **1a**, which on the basis of substrate reactivity appeared to be the most reactive neutral d<sup>8</sup> complex toward oxidative addition<sup>2,3</sup> yet described. Studies of **1a** were complicated by insolubility and side reactions of the hydrogen bridge. We have circumvented these difficulties by preparing **1b**<sup>4,5</sup> which is more soluble and has a BF<sub>2</sub> bridge. Herein we describe the rates for reactions between **1b** and alkylating agents (eq 1). These



studies have uncovered evidence for a cationic intermediate and an unexpected neighboring group effect.

Alkyl halides and sulfonates react smoothly with **1b** affording trans rhodium(III) adducts **2** (eq 1). The rates for these reactions were followed spectrophotometrically at 560 or 522 nm where the pale yellow products have no absorbance. The rate law follows a well-defined second-order behavior

$$\frac{d[\text{Rh(III)}]}{dt} = k_2[\text{Rh(I)}][\text{RX}]$$

All products listed were isolated in >65% yield and fully characterized by elemental analyses and pmr (demonstrating trans stereochemistry). Rate comparisons for reaction of methyl iodide with neutral d<sup>8</sup> complexes show **1b** to be ~10<sup>4</sup> more reactive than any neutral d<sup>8</sup> complex of which we are aware.<sup>6</sup>

That these reactions proceed through a cationic rhodium(III) complex is demonstrated by the observation that treatment of **1b** with *n*-butyl bromide in the presence of LiCl affords *only* the trans chloro rhodium alkyl **2** (R = *n*-butyl, X = Cl). Under the same conditions the trans bromo alkyl **2** (R = *n*-butyl, X = Br) does not exchange with LiCl. Evidence for such an intermediate has been sought without success in oxidative additions of Vaska's complex.<sup>7</sup> A solvated cationic complex, [CH<sub>3</sub>Rh(C<sub>2</sub>DOBF<sub>2</sub>)·NCCH<sub>3</sub>]<sup>+</sup>BPh<sub>4</sub><sup>-</sup>, has been isolated and characterized by treating the methyl

(1) J. P. Collman, D. W. Murphy, and G. Dolcetti, *J. Amer. Chem. Soc.*, **95**, 2687 (1973).

(2) (a) J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, **88**, 3504 (1966); (b) J. P. Collman and W. R. Roper, *Advan. Organometal. Chem.*, **7**, 54 (1968).

(3) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

(4) The rhodium(III) dichloride, **2** (R = Cl, X = Cl) (H in place of BF<sub>2</sub>), was prepared by treating RhCl<sub>3</sub>·H<sub>2</sub>O and LiCl in boiling ethanol under a stream of CO with the new ligand [3,3'-(trimethylenedinitrilo)-di-2-pentanone dioximate] (prepared by condensation of 3-oximino-2-pentanone<sup>6</sup> with 1,3-propanediamine). The dichloride was treated with boron trifluoride etherate to yield **2** (R = Cl, X = Cl) which was reduced in aqueous basic ethanol affording **1b** as very air-sensitive green lustrous crystals.

(5) A. F. Ferris, *J. Org. Chem.*, **24**, 1726 (1959).

(6) M. Kubota, G. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, **7**, 195 (1973), and references therein.

(7) R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970).

tosylate adduct **2** (R = CH<sub>3</sub>, X = OTs) with NaBPh<sub>4</sub> in acetonitrile.

The order of substrate reactivities shown in Table I

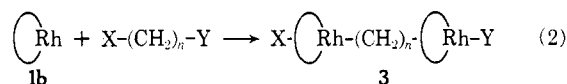
Table I. Second-Order Rate Constants for Reactions of **1b** (eq 1, 2)

Substrate	10 <sup>3</sup> k, <sup>a</sup> M <sup>-1</sup> sec <sup>-1</sup>	Substrate	10 <sup>3</sup> k, <sup>a</sup> M <sup>-1</sup> sec <sup>-1</sup>
CH <sub>3</sub> I	10 <sup>b</sup>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> Cl	0.006
CH <sub>3</sub> CH <sub>2</sub> I	5500 <sup>b</sup>	Br(CH <sub>2</sub> ) <sub>2</sub> Br	23 <sup>b,c</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> I	1400 <sup>b</sup>	Br(CH <sub>2</sub> ) <sub>3</sub> Br	17 <sup>c</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> I	1800 <sup>b</sup>	Br(CH <sub>2</sub> ) <sub>4</sub> Br	13 <sup>c</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	8.6	Br(CH <sub>2</sub> ) <sub>5</sub> Br	12 <sup>c</sup>
(CH <sub>3</sub> ) <sub>2</sub> CHBr	0.034	Br(CH <sub>2</sub> ) <sub>2</sub> Cl	12 <sup>d</sup>
CH <sub>3</sub> OTs	54	Cl(CH <sub>2</sub> ) <sub>2</sub> Cl	0.005 <sup>e</sup>
CH <sub>3</sub> CH <sub>2</sub> OTs	1.9 <sup>b</sup>	Cl(CH <sub>2</sub> ) <sub>3</sub> Cl	0.015 <sup>d,e</sup>
		I(CH <sub>2</sub> ) <sub>2</sub> Cl	1600 <sup>d</sup>

<sup>a</sup> T = 25 ± 2°, THF, [**1b**] ≈ 1 × 10<sup>-4</sup> M for iodides, [**1b**] ≈ 1 × 10<sup>-3</sup> M for bromides, chlorides, and tosylates. <sup>b</sup> For these representative cases pseudo-first-order conditions were employed. Using the alkylating agent in >tenfold excess and varying this concentration over at least a tenfold range did not change the calculated second-order rate const. <sup>c</sup> k<sub>2(obsd)}/4. <sup>d</sup> k<sub>2(obsd)}/2. <sup>e</sup> In this instance the sole product isolated was the monorhodium product **2** (R = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Cl, X = Cl).</sub></sub>

strongly implies nucleophilic (S<sub>N</sub>2) attack at carbon by rhodium (a two-electron reaction). The order methyl > ethyl > secondary > cyclohexyl supports this hypothesis. The order I > OTs ~ Br > Cl might be explained either by a one-electron or a two-electron mechanism,<sup>8</sup> but 1-bromo adamantane fails to react even after 4 days at 80°. Such rate data together with the evidence for a cationic intermediate strongly support the view that these oxidative additions involve initial nucleophilic attack by rhodium. A stereochemical test of this mechanism has thus far been thwarted by a rapid rhodium-rhodium exchange between **1b** and **2**.<sup>9</sup>

We have further noted a remarkable neighboring group effect when **1b** is treated with α,ω-dihalo alkyls (eq 2). For X = Y = Br and n = 2, 3, 4, or 6, the *sole*



product (isolated in >65% yield) is the bis rhodium complex **3**. When 1,10-dibromodecane is used, we find nearly equivalent amounts of **3** (n = 10, X = Y = Br) and the monomeric product **2** (R = CH<sub>2</sub>(CH<sub>2</sub>)<sub>8</sub>CH<sub>2</sub>-Br, X = Br). Again these reactions follow a second-order rate law. The second-order rate constants for α,ω-dihalides are little different from those of analogous simple alkyl halides when account is taken of statistical factors (Table I). We have thus concluded that the second oxidative addition is much faster than the first which shows modest rate enhancement. Even 1-iodo-2-chloroethane forms **3** (n = 2, X = I, Y = Cl) as the major product<sup>10</sup>—a surprising result in view of the 10<sup>6</sup> rate difference between iodides and chlorides. Similarly 1-bromo-2-mesyethane yields **3** (n = 2, X = Br, Y = OMs) as the major product—a result suggesting

(8) We are unaware of alkyl sulfonates reacting in a one-electron process.

(9) We have studied this reaction independently. Both primary and secondary addition products of **1a** were found to exchange the alkyl group in the presence of **1b** affording a mixture of the starting material and the new alkyl complex, **2**.

(10) Smaller amounts of **2** (R = I, X = I) and **2** (R = Cl, X = I) were also obtained.

that the rapid second reaction is also a two-electron change. The failure of 1,4-dibromocyclohexane to yield any product other than the monorhodium adduct **2** (R = 4-bromocyclohexyl, X = Br) implies a cyclic intermediate in this neighboring group effect.

As far as we are aware, such a neighboring group effect by a d<sup>6</sup> center is unparalleled.<sup>11</sup> Experiments are in progress to further explore this remarkable effect.

**Acknowledgment.** This work was supported by the National Science Foundation grant GP20273X. We are indebted to J. Brauman for helpful discussions.

(11) An electrophilic neighboring group effect has been observed over five carbons: R. K. Summerbell and S. R. Forrester, *J. Org. Chem.*, **26**, 4834 (1961); P. E. Peterson, D. R. Bonazza, and P. M. Herichs, *J. Amer. Chem. Soc.*, **95**, 2222 (1973). A referee has brought to our attention a report of a similar result in the reaction between vitamin B<sub>12</sub> and Br(CH<sub>2</sub>)<sub>4</sub>Br: E. L. Smith, L. Mervyn, and P. W. Muggleton, *Ann. N. Y. Acad. Sci.*, **112**, 565 (1964).

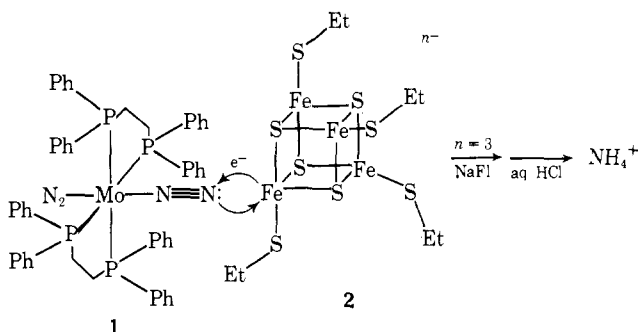
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### Biological and Abiological Nitrogen Fixation by Molybdenum-Bound N<sub>2</sub>/4Fe-4S Cluster Systems

Sir:

Through study of the Mo-<sup>15</sup>N<sub>2</sub> coordination compound **1**<sup>1</sup> and a new ferredoxin model, the 4Fe-4S cluster **2**,<sup>2</sup> we have discovered a biogenetic-type reaction



in which the cluster and reducing agent produce <sup>15</sup>NH<sub>3</sub> from **1**, apparently by direct action on the N<sub>2</sub> ligand. This abiological reaction, although proceeding in small yield, is novel and carries distinct implications for the chemical nature of the biological N<sub>2</sub> fixation process.

In order to identify the particular reduced 4Fe-4S cluster species involved in the N<sub>2</sub> fixation process, the redox properties of the bis(tetraethylammonium) salts were delineated by cyclic voltammetry.<sup>3a</sup> A reversible one-electron reduction of 2<sup>2-</sup> to 2<sup>3-</sup> was observed [CH<sub>3</sub>CN, E<sub>1/2</sub> = -1.30 V vs. saturated calomel electrode (sce); DMSO, -1.28 V; 1-methyl-2-pyrrolidinone (NMP), -1.31 V]. Continued cathodic scan-

(1) (a) Prepared according to T. A. George and C. D. Seibold, *J. Organometal. Chem.*, **30**, C13 (1971), and labeled by subsequent exchange with <sup>15</sup>N<sub>2</sub>. (b) Structure: T. Uchida, Y. Uchida, M. Hidai, and T. Kodama, *Bull. Chem. Soc. Jap.*, **44**, 2883 (1971).

(2) (a) Preparation: B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 3523 (1973). (b) X-Ray structure of -SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> homolog: T. Herskovitz, B. A. Averill, R. H. Holm, J. H. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2437 (1972).

(3) (a) Measurements were conducted at room temperature at sweep rates from 60 to 220 mV/sec in 0.1 M tetraethylammonium perchlorate solutions using a Pt button indicator electrode. (b) Peak separations for the couples 2<sup>2-</sup> ⇌ 2<sup>3-</sup> and 2<sup>3-</sup> ⇌ 2<sup>4-</sup> were identical and the ratio of anodic to cathodic currents one, within experimental error.

ing revealed further conversion to 2<sup>4-</sup>, which was completely reversible in NMP (-1.96 V).<sup>3b</sup> Irreversible oxidation of 2<sup>2-</sup> was noted near -0.10 V on anodic sweeps.

For chemical generation of the 2<sup>n-</sup> entities needed for fixation experiments, a series of homogeneous radical anion reductants were auditioned (standard oxidation potentials in 1,2-dimethoxyethane vs. sce):<sup>4</sup> sodium naphthalene (NaNp, 2.60 V), sodium phenanthrene (NaPh, 2.48 V), sodium pyrene (NaPy, 2.10 V), sodium anthracene (NaAn, 1.98 V), sodium fluoranthene (NaFl, 1.77 V), and sodium acenaphthylene (NaAc, 1.65 V). As inferred from the redox potentials and as evidenced by potentiometric and/or chemical data, stoichiometric amounts of NaNp or NaPh converted 2<sup>2-</sup> completely to 2<sup>4-</sup>. With NaPy or NaAn an equilibrium mixture of 2<sup>3-</sup> and 2<sup>4-</sup> was formed, while NaFl or NaAc served only to generate 2<sup>3-</sup>. The reductions were carried out both in THF, in which 2<sup>3-</sup> and 2<sup>4-</sup> showed partial solubility, or under completely homogeneous conditions in NMP.<sup>5</sup>

As to the effect of a 4Fe-4S cluster itself, we note that 2<sup>2-</sup>, 2<sup>3-</sup>, and 2<sup>4-</sup> separately and *per se* fail to produce NH<sub>3</sub> from excess or stoichiometric amounts of N<sub>2</sub> in THF.<sup>6</sup> Fixation experiments with 2<sup>3-</sup> and 2<sup>4-</sup> were also carried out by starting with THF suspensions of 2<sup>2-</sup>, saturated and blanketed with <sup>14</sup>N<sub>2</sub> or <sup>15</sup>N<sub>2</sub>, to which were added *ca.* 200 equiv of the desired radical anion. Yields (mol of NH<sub>3</sub>/mol of 2<sup>2-</sup>) thus obtained (NaNp, 0.275; NaPh, 0.163; NaPy, 0.015-0.000; NaAn, NaFl, NaAc, 0.000) reveal the involvement of 2<sup>4-</sup> in the overall fixation process and the inability of 2<sup>3-</sup> to fix excess N<sub>2</sub> under any conditions assayed.<sup>7</sup> Similarly, <sup>15</sup>N<sub>2</sub> or <sup>15</sup>N-labeled **1** is converted by [Fe<sub>4</sub>S<sub>4</sub>(S<sub>2</sub>C<sub>2</sub>Ph<sub>2</sub>)<sub>4</sub>] (**3**) and *ca.* 200 equiv of NaNp to <sup>15</sup>NH<sub>3</sub>.<sup>8</sup> However, no <sup>15</sup>NH<sub>3</sub> is produced from <sup>15</sup>N<sub>2</sub> or <sup>15</sup>N-labeled **1** in the presence of 2 equiv of **3** pretreated with only 8-16 equiv of NaNp. Even in the presence of O<sub>2</sub>, cluster 2<sup>4-</sup> and excess NaNp effect NH<sub>3</sub> formation (0.070-0.120 mol) from free N<sub>2</sub>.

In the multicomponent reaction, a 100 ml THF suspension of 0.03 mmol <sup>15</sup>N-labeled **1** and 0.45 mmol 2<sup>3-</sup> was allowed to react for 12 hr under argon, after which 9 mmol of NaFl in 50 ml of THF was added. After

(4) Prepared by mixing equimolar quantities of sodium and the hydrocarbon in THF. For the oxidation potential measurements, see G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *Recl. Trav. Chim. Pays-Bas*, **75**, 487 (1956).

(5) (a) Reduction of 2<sup>2-</sup> with excess Na sand followed by filtration was found to be a superior procedure for the production of NMP solutions of 2<sup>4-</sup>. (b) All fixation experiments employed the bis(tetraphenylarsonium) 2<sup>2-</sup> species as starting material.

(6) (a) All experiments were conducted at room temperature for 12 hr to 3 days in a closed creased flask in which the appropriate blanketing gas continually recirculated through the reaction mixture. For design and details, see J. A. Gladysz, Ph.D. Thesis, Stanford University, 1974, in preparation. (b) All <sup>14</sup>N<sub>2</sub> experiments were worked up as described in ref 8, employing a Kjeldahl-type distillation-titration followed by, after reconcentration of the sample, either a potentiometric determination using an Orion Model 95-10 NH<sub>3</sub> gas electrode or colorimetric analysis with Nessler's reagent. (c) Yields of <sup>15</sup>NH<sub>4</sub>Cl were determined by cocrystallization with natural abundance NH<sub>4</sub>Cl prior to the Kjeldahl work-up, followed by conversion to N<sub>2</sub> with alkaline NaOBr and precise mass spectrometric measurement of the <sup>29</sup>(N<sub>2</sub>)/<sup>28</sup>(N<sub>2</sub>) peak ratio.

(7) (a) Gas absorption was noted in experiments with NaNp but not NaFl; upon titration of 2<sup>2-</sup> with NaNp uptake usually commenced near the third equivalent added. Exhaustive controls have established that the cluster decomposition products formed in the presence of large excesses of NaNp are inactive in the fixation process. (b) Identical behavior was observed with (Ph<sub>3</sub>As)<sub>2</sub>[Fe<sub>4</sub>S<sub>4</sub>(SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] in this type of experiment with NaNp. (c) Hydrazine was not observed in these or any other experiments.

(8) E. E. van Tاملen, J. A. Gladysz, and J. S. Miller, *J. Amer. Chem. Soc.*, **95**, 1347 (1973).