Electron Transfer. 27. Catalytic Sequences in Which All Steps Are Outer Sphere[1]
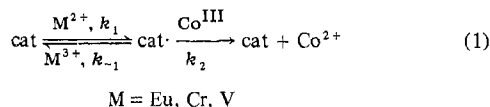
Y.-T. FANCHIANG and EDWIN S. GOULD*

Rates of electron-transfer reactions, as catalyzed externally by derivatives of 4,4'-bipyridyl and 1,2-dipyridylethylene, are compared. Oxidants are $(en)_3Co^{3+}$ and $(NH_3)_5pyCo^{3+}$; reductants are Eu^{2+}, V^{2+}, and Cr^{2+}. In 1.0 M $HClO_4$, catalysts have no available lead-in substituents, and all steps in the catalytic sequences are outer sphere. Data conform to sequence 1, in which the catalyst is reduced by M^{2+} (k_1) to a radical cation intermediate, after which the intermediate may be oxidized either by M^{3+} (k_{-1}) or by Co(III) (k_2). Reductions by Eu^{2+} of catalysts in this study are 10^{-4} to 10^{-2} times as rapid as reductions of catalysts derived from 4-pyridinecarboxylic and 2,4-pyridinedicarboxylic acids. Among the Eu^{2+}–$Co(en)_3^{3+}$ reactions, k_2/k_{-1} ratios are very nearly independent of catalyst, whereas the pattern of k_1 values for the different reducing centers corresponds closely to the pattern of specific rates for uncatalyzed outer-sphere reductions by these centers. Thus, electron transfer from reductant to catalyst, as well as that from catalyst to oxidant,[2c] conforms to Marcus's model.[12] Kinetic measurements on systems catalyzed by methylviologen (I), in conjunction with the redox potential, −0.515 V, for that catalyst in 1 M ClO_4^-, allow calculation of the specific rates at which the radical intermediate reacts with each of the three M^{3+} centers and with $Co(en)_3^{3+}$. The trend in k_{-1} values is in the same direction as that in k_1, but is somewhat more marked, suggesting that reorganizational barriers related to those associated with the conversion of M^{2+} to M^{3+} in solution also impede the reverse processes. As a result of the relatively low values of k_{-1} for chromium and europium, inhibition of the catalyzed Cr^{2+} reductions by Cr^{3+} is suppressed, and the analogous inhibition in the europium system can be observed only when $(Eu^{3+}) > 100(Co^{III})$.

The outer-sphere reductions of $(NH_3)_6Co^{3+}$, $(NH_3)_5pyCo^{3+}$, $(en)_3Co^{3+}$, and related oxidants by Cr^{2+}, Eu^{2+}, and V^{2+} are strongly catalyzed by such pyridine derivatives as isonicotinamide, 4-pyridylacrylic acid, and 2,4-pyridinedicarboxylic acid.[2] A variety of such catalyzed reactions have been shown to proceed through the sequence[2a,c,d]

$$\text{cat} \underset{M^{3+},\, k_{-1}}{\overset{M^{2+},\, k_1}{\rightleftharpoons}} \text{cat} \cdot \xrightarrow[k_2]{Co^{III}} \text{cat} + Co^{2+} \qquad (1)$$

$$M = Eu, Cr, V$$

where "cat·" is a substituted pyridyl radical, present at small steady-state concentrations. Kinetic experiments under steady-state conditions generally allow calculation of k_1 and k_2/k_{-1}, but additional data, such as an independent estimate[3] of k_2 or an equilibrium constant for the initial reduction of the catalyst, are needed to obtain all three specific rates.

More than 20 catalysts have thus far been examined. These exhibit a wide variety of structural features and a range of activities, but virtually all have at least one exposed donor function, leading to several complications. Catalysts and the radicals formed from them may exist in protonated and nonprotonated forms, each reacting at its own specific rate, and the partition between these forms, both at the oxidized and the reduced level, is a function of acidity.[4] This means individual rate constants obtained at a single acidity do not necessarily apply to single species but, assuming proton transfers to be very rapid, are weighted averages of the specific rates associated with two or more species. The availability of basic sites on the catalyst also adds an element of mechanistic ambiguity with respect to the initial step, for this process, as well as its reversal, may proceed by an outer-sphere path, a bridged route, or a combination of the two.[5] A substantial inner-sphere contribution to the reduction of the catalyst by Cr^{2+} may convert the catalyst, partially or completely, to a substitution-inert Cr(III)-catalyst complex having catalytic properties different from those of the unbound catalyst.

Catalysts used in the present work, although somewhat less powerful than those previously encountered,[2d] were chosen to minimize these uncertainties.

Experimental Section

Materials. Solutions of europium(II),[6] vanadium(II),[7] and chromium(II)[8] were prepared by published procedures. Cobalt(III)

complexes were available from a previous study.[2c] N,N'-Dimethyl-1,2-bis(4-pyridyl)ethylene diiodide was prepared by the methylation procedure of Rembaum[9] and converted to the corresponding perchlorate by passage through a column of anion-exchange resin (AG 2X8 200–400 mesh) in the perchlorate form. Other catalysts (Aldrich or Alfred Bader products) were used as received.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[2c,6] All reactions were carried out under nitrogen. All catalyzed reactions were first order each in reductant and catalyst. Reductions by Cr^{2+} and Eu^{2+} were carried out with the ratio $(red)/(Co^{III})$ greater than 10, but for a number of reductions by V^{2+} the oxidant was held in excess. Under our conditions, reductions by Cr^{2+} followed pseudo-zero-order kinetics with rates independent of the concentration of the Co(III) complex and its identity. Such reductions were unaffected by added Cr^{3+}. In contrast, reductions using V^{2+} were first order in Co(III) and were inhibited by V^{3+}, whereas with excess oxidant rates were independent of Co(III). The kinetic character of the Eu^{2+} reductions was generally analogous to that of the Cr^{2+} reductions. However, when the Eu^{2+}–$Co(en)_3^{3+}$ reaction was carried out in the presence of >0.1 M Eu^{3+}, it exhibited pseudo-first-order curves and was inhibited by Eu^{3+}. Rates with all reductants were not significantly dependent on acidity in the range 0.1–1.0 M H^+. Most measurements employed 1.0 M $HClO_4$ as a supporting electrolyte, but a few reactions were run in $HClO_4$–$LiClO_4$ mixtures. To evaluate the effects of large variations in (Eu^{3+}), a series of runs was carried out with added $Eu(ClO_4)_3$ + $Al(ClO_4)_3$, keeping the total concentration of tripositive ions at 0.4 M. Pseudo-first-order reactions were followed to at least five half-lives and rate constants were obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time. Pseudo-first-order rate constants derived from replicate runs checked to within 7% and pseudo-zero-order constants within 5%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments. For those reactions catalyzed by methylviologen and 4,4'-bipyridyl, the drop in absorbance at 465–495 nm, representing the primary reaction, was followed by an increase, reflecting formation of the radical intermediate in greater than steady-state amounts after the Co(III) oxidant had been exhausted. This second reaction did not seriously complicate interpretation of the results.

Potentiometric Experiments. The reduction potential of methylviologen (I) was determined in 1.0 M $HClO_4$ by estimating the extent of conversion to the reduced form in various known mixtures of Eu^{2+} and Eu^{3+}. Measurements were carried out at 604 nm, at which wavelength the reduced (radical) form has an extinction coefficient[10] 1.2×10^4 and the oxidized form a negligible absorptivity. The average of four such measurements, in conjunction with the standard potential −0.379 V reported for the Eu^{2+}/Eu^{3+} couple in similar medium,[11] yielded $E = -0.515 \pm 0.004$ V. Similar measurements were not

Table I. Kinetic Data for Reductions of Co(en)$_3^{3+}$, As Catalyzed by Methylviologen[a]

Reductant, M^{2+}	$10^3 \times$ [Co^{III}], M	$10^2 \times$ [M^{2+}], M	$10^3 \times$ [cat], M	$10^2 \times$ [M^{3+}], M	k[b]
Pseudo-zero-order reductions Cr^{2+}	1.18	1.90	3.60	0	2.9
	1.18	3.80	3.60	0	5.8
	1.31	2.19	3.33	0	2.9
	1.31	2.19	6.67	0	6.0
	1.31	2.19	13.3	0	14
	1.18	3.80	1.80	0	2.9
	0.78	4.00	3.30	0	5.7
	1.56	4.00	3.30	0	5.7
	1.18	1.90	3.60	3.8	3.2
	1.18	1.90	3.60	20	4.0
	1.95[c]	4.00	3.30	0	5.6
Eu^{2+}	1.18	2.00	1.45	0	17
	1.18	4.00	1.45	0	39
	1.18	2.00	0.73	0	8.6
	1.18	2.00	1.45	4.0	17
	0.78	2.00	1.45	0	18
Pseudo-first-order reductions Eu^{2+}	0.78	2.0	1.61	20[d]	22
	0.78	2.0	1.61	30[e]	16
	0.78	2.0	1.61	40	12
V^{2+}	21.2	0.20	5.40	0	12
	19.2	0.20	2.70	0	6.2
	13.5	0.20	2.70	0	6.2
	1.04	1.97	3.47	0.985	7.9

[a] Reactions at 25 °C. Except for the first-order reductions of Eu^{2+}, the supporting electrolyte was 1.0 M HClO$_4$. [b] Pseudo-zero-order rate constants are in M s^{-1} × 10^6. Pseudo-first-order rate constants are in s^{-1} × 10^3. [c] Oxidant was (NH$_3$)$_5$Co(py)$^{3+}$. [d] [Al^{3+}] = 0.20 M. [e] [Al^{3+}] = 0.10 M.

possible for 4,4-bipyridyl, the reduced form of which decomposed rapidly in our medium.

Results and Discussion

Reactions proceed by a combination of catalyzed and uncatalyzed paths. If we apply the steady-state approximation to the radical intermediate, cat·, mechanism 1 yields the rate law[2a,c,d]

$$\text{rate} = \frac{k_1 k_2 [\text{Co}^{III}][\text{M}^{2+}][\text{cat}]}{k_{-1}[\text{M}^{3+}] + k_2 [\text{Co}^{III}]} + k_{un}[\text{Co}^{III}][\text{M}^{2+}] \quad (2)$$

The k_{un} term describes the uncatalyzed reaction, which may be considered negligible at the catalyst concentrations here employed. Observed kinetic behavior is dependent on the competition between M^{3+} and the Co(III) oxidant for the intermediate, cat·, as reflected in the denominator of eq 2. When the k_{-1} term, arising from reversal of the initial step, is dominant, the catalyzed reaction is first order in Co(III) and is inhibited by M^{3+}. When the k_2 term, representing

reaction of intermediate cat· with Co(III), is large, the rate becomes independent of (Co^{III}) and approaches k_1(M^{2+})(cat), the rate of electron transfer to the catalyst.

Typical kinetic data, referring to the reductions of Co(en)$_3^{3+}$, as catalyzed by methylviologen, I, appear in Table I. For the
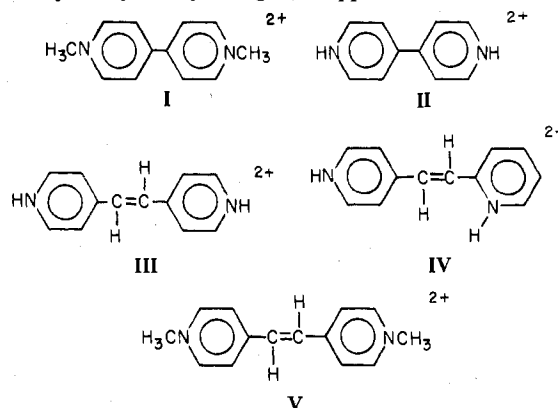
pseudo-zero-order reactions with reductant in excess, plots of the observed rates vs. the product [M^{2+}][cat] are linear with slope k_1, whereas plots of pseudo-first-order rate constants vs. the quotient [M^{2+}][cat]/[M^{3+}] are linear with slope $k_1 k_2/k_{-1}$. Values of k_1 and the ratio k_2/k_{-1} are summarized in Table II. Only k_1 was obtained experimentally for Cr^{2+} reductions, since k_{-1}[Cr^{3+}] falls far below k_2[Co^{III}] in all cases. With Eu^{2+} as reductant, k_1[Eu^{3+}] can be made to exceed k_2[Co^{III}] when the oxidant is Co(en)$_3^{3+}$, but not when it is the more rapidly reacting[2c] (NH$_3$)$_5$CoH$_2$O^{3+} or Co(NH$_3$)$_5$Co(py)$^{3+}$; hence k_2/k_{-1} values are entered only for the chelated oxidant. In cases where comparison is possible, k_1, referring to electron transfer to the catalyst, is, as expected, independent of the Co(III) oxidant taken. Note that k_1 values for the present catalysts lie below those for isonicotinic acid and its amide (the protype electron-transfer catalysts[2a,b]) by about 10^2 and below those for 2,4-pyridinedicarboxylato derivatives, the most powerful group of catalysts thus far encountered,[2d] by approximately 10^4.

Among the catalyzed Eu^{2+}–Co(en)$_3^{3+}$ reactions, the k_2/k_{-1} ratios fall into a very narrow range, thus conforming to the Marcus model, which predicts that the relative rates of outer-sphere oxidation of a given reductant by two or more oxidants should be the same for a series of reductants.[12] Considerably greater variation in this ratio has been observed[2d] for catalysts featuring "lead-in" donor groups which allow the operation of an inner-sphere component in the initial step. Moreover, comparing k_1 values for the different reducing

Table II. Catalyzed Reductions of Cobalt(III) Complexes. Kinetic Parameters[a]

Catalyst	Oxidant	Eu^{2+} k_1	Eu^{2+} k_2/k_{-1}	V^{2+} k_1	V^{2+} k_2/k_{-1}	Cr^{2+} k_1	Cr^{2+} k_2/k_{-1}
Methylviologen (I)	Co(en)$_3^{3+}$	0.66	3.9 × 10^2	2.3	0.49	0.043	(1.9 × 10^4)[f]
	(NH$_3$)$_5$Co(py)$^{3+}$	0.76				0.042	
	(NH$_3$)$_5$CoH$_2$O^{3+}	0.69				b	
4,4'-Bipyridyl (II)	Co(en)$_3^{3+}$	0.37	3.3 × 10^2	1.4	0.47	0.025	(1.6 × 10^4)[f]
	(NH$_3$)$_5$Co(py)$^{3+}$	0.45					
	(NH$_3$)$_5$CoH$_2$O^{3+}	0.48					
1,2-Bis(4-pyridyl)ethylene (III)[e]	Co(en)$_3^{3+}$	0.22	6.9 × 10^2			0.015	(3.2 × 10^4)[f]
1-(2-Pyridyl)-2-(4-pyridyl)-ethylene (IV)	Co(en)$_3^{3+}$	0.31	2.5 × 10^2				
1-(3-Pyridyl)-2-(4-pyridyl)-ethylene	Co(en)$_3^{3+}$	c					
N,N'-Dimethyl-1,2-bis(4-pyridyl)-ethylene (V)	Co(en)$_3^{3+}$	0.36[d]					

[a] Values of k_1 (see mechanism 1) are in M^{-1} s^{-1}. The ratio k_2/k_{-1} is dimensionless. Reaction temperatures were 25 °C. Reactions were generally carried out in 1.0 M HClO$_4$. [b] Value could not be determined because of the rapid (inner sphere) reaction of Cr^{2+} and Co(NH$_3$)$_5$-OH^{2+}. [c] Not an active catalyst. [d] Reactions with this sparingly soluble catalyst were carried out in 0.12 M HClO$_4$. [e] For evidence that this catalyst is a trans olefin, see T. Katsumoto, *Bull. Chem. Soc. Jpn.*, **33**, 1376 (1960). [f] Estimated values (see text).

Table III. Reductions of Co(en)$_3$$^{3+}$, As Catalyzed by Methylviologen. Specific Rates for Individual Steps^a

Reductant	V^{2+}	Eu^{2+}	Cr^{2+}
$E°$, V	-0.242^b	-0.379^c	-0.41^d
K_1 (=k_1/k_{-1})	2.5×10^{-5}	5.0×10^{-3}	1.7×10^{-2}
k_1	2.3	0.66	0.043
k_{-1}	9×10^4	1.3×10^2	2.6
k_2		5.1×10^4	

^{a} Values of k_1, k_{-1}, and k_2 (see mechanism 1) are in M^{-1} s^{-1}. Reaction temperatures were 25 °C. Reactions were carried out in 1.0 M HClO$_4$. ^{b} This work. ^{c} Reference 11. ^{d} Reference 15.

centers, we find the V^{2+}/Eu^{2+} ratios (3.5–3.8) and the Eu^{2+}/Cr^{2+} ratios (each 15) to correspond closely to the ratios of specific rates observed for uncatalyzed outer-sphere reductions by these metal ions,[6a,b,13] again in agreement with the Marcus picture.

Although reductions of the catalysts (k_1) are somewhat faster for V^{2+} than for Eu^{2+}, the competition between Co^{III} and M^{2+} for the intermediate cat· (k_2/k_{-1}) is seen to be much more favorable for the europium systems. Since k_2 is independent of the reductant taken, the reversal of the initial step, k_{-1}, must be about 10^3 as rapid for the vanadium reductions as for europium and the ratio k_1/k_{-1}, the equilibrium constant for the initial step, 400 times as great for Eu^{2+}, the latter difference being a direct reflection of the more negative potential associated with the lanthanide center. The kinetic parameters listed for the Co(en)$_3$$^{3+}$ reductions (as catalyzed by methylviologen), in combination with the standard potential -0.379 V reported for the Eu^{2+}/Eu^{3+} couple in 1 M aqueous perchlorate,[11] lead to a potential of -0.242 V for the V^{2+}/V^{3+} couple in that medium, comparable to the value -0.255 V estimated for that half-reaction in aqueous sulfate.[14] In addition, we may use the standard Cr^{2+}/Cr^{3+} potential, -0.41 V,[15] to approximate the k_2/k_{-1} ratios for several of the catalyzed Cr^{2+}–Co(en)$_3$$^{3+}$ reactions. These ratios (Table II) exceed 10^4, thus being consistent (see eq 2) with our observation that rates of the catalyzed Cr^{2+} reductions are independent of (Co^{III}), even at the highest practical concentrations of added Cr^{3+}.

The redox potential determined for methylviologen in our medium, -0.515 V, may be compared with the value -0.47 V reported for this cation in solutions of very low ionic strength (0.015 M).[16] The shift to the more negative values at high ionic strength agrees, in both magnitude and direction, with that predicted for reduction of a di- to a unipositive species.[17] The present potential for the catalyst allows us to estimate equilibrium constants for the initial electron-transfer steps (K_1 = k_1/k_{-1}) associated with the three reductants. From the measured k_1 values, we may then calculate individual values of k_{-1} (Table III) and from the latter, in conjunction with our experimental k_2/k_{-1} ratios, k_2. Note that the k_{-1} values lie in the same order as those for k_1; i.e., the most rapid trivalent oxidant, V^{3+}, is derived from the most rapid divalent reductant, V^{2+}. However, the trend among the 3+ species is the more marked. The kinetic advantage which V^{2+} enjoys over Cr^{2+} in outer-sphere reactions has been noted many times and has been attributed to the relatively greater alteration of configuration associated with removal of an antibonding e$_g$ electron of Cr^{2+}.[18] A similar reorganizational barrier should impede the addition of an e$_g$ electron to Cr^{3+}, but it should be more pronounced, for in addition to the Jahn–Teller distortion there will be unfavorable interaction between the incoming electron and the axially coordinated water molecules.[19] A barrier of intermediate magnitude should be associated with the Eu^{2+}/Eu^{3+} couple. The Jahn–Teller distortion resulting from removal of an antibonding 4f electron from a half-filled subshell when Eu^{2+} is converted to Eu^{3+} would be expected to be small since overlap between anti-

bonding f orbitals and ligands in a system of coordination number 8 or 9[20a] is considerably less severe than that between antibonding d orbitals and ligands in octahedral systems.[20b]

From the difference in k_{-1} values, we see also why reductions by V^{2+} in the present series are inhibited by V^{3+} whereas those by Cr^{2+} are not inhibited by Cr^{3+}. Because of the low k_{-1} for Cr^{2+}, the "inhibition term", k_{-1}(M^{3+}), in the denominator of eq 2 becomes significant only when (Cr^{3+}) exceeds 10^4(Co^{III}), whereas in the case of vanadium, the two terms are comparable when (V^{3+}) = $^1/_2$(Co^{III}). For europium, with an intermediate value of k_{-1}, inhibition by Eu^{3+} is appreciable when (Eu^{3+}) > 10^2(Co^{III}).[21-23]

In sum, although the outer-sphere sequences examined here conform to the same general kinetic picture as that applying to catalyses in which the initial act is an inner-sphere process, electron transfer to and from the catalyst in the present systems is considerably more sluggish, resulting in a greater delay in reaching steady state and, in some instances, suppression of the usual inhibition by M^{3+}. In addition, the competition between Co(III) and M^{3+} for the reactive intermediate is much less sensitive to catalyst structure than is the case for catalysts having bridging substituents, and the relative rates for reduction of the catalyst by Eu^{2+}, V^{2+}, and Cr^{2+} are found closely to follow those for uncatalyzed outer-sphere reductions by these centers. Finally, our experiments suggest a kinetic pattern for outer-sphere oxidations by Eu^{3+}, V^{3+}, Cr^{3+}, and Co(en)$_3$$^{3+}$, but whether this pattern will persist in noncatalytic systems remains to be determined.

Registry No. Co(en)$_3$$^{3+}$, 14878-41-2; (NH$_3$)$_5$Co(py)$^{3+}$, 31011-67-3; (NH$_3$)$_5CoH_2$O^{3+}, 14403-82-8; Cr^{2+}, 22541-79-3; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3; I, 4685-14-7; II, 46040-54-4; III, 17126-00-0; IV, 17126-02-2; V, 46740-72-1.

References and Notes

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(19) An analogous reorganizational barrier should retard the reduction of low-spin cobalt(III). Thus, Co(en)$_3$$^{3+}$ and V^{3+} are found (Table III) to react with the methylviologen radical at very nearly the same rate although the cobalt complex is by far the stronger oxidant. We thank a reviewer for calling our attention to this point.
(20) (a) For a review of coordination numbers and geometries in lanthanide systems, see T. Moeller, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **7**, 275 (1972); (b) see, for example, H. G. Friedman, Jr., G. R. Choppin,

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(21) It is also clear that the inability of methylviologen and related molecules to catalyze reductions of Co(III) by Ru(NH₃)₆²⁺ is simply a reflection of the weak reduction potential (+0.214 V)[6] of the latter.[22] The equilibrium constant for reduction of methylviologen by this reductant is only 9 × 10⁻¹³. A maximum value of 10⁸ M⁻¹ s⁻¹ for k_1 (the diffusion-controlled limit for bimolecular reactions between +1 and +3 ions[23]) corresponds

to an upper limit of 9 × 10⁻⁵ M⁻¹ s⁻¹ for k_1. In contrast, the specific rate for the uncatalyzed reduction of Co(en)₃³⁺ by Ru(NH₃)₆²⁺ is approximately 6 × 10⁻³ M⁻¹ s⁻¹,[13] and other Co(III) derivatives are reduced still more rapidly.
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Synthesis and Some Oxidation Reactions of [Bis(trimethylsilyl)amino]dimethylphosphine

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The synthesis, characterization, and some reactions of [bis(trimethylsilyl)amino]dimethylphosphine (**1**) are reported. Although compound **1** was routinely prepared via the reaction of LiN(SiMe₃)₂ and Me₂PCl, it was also isolated when Me₃SiPMe₂ was treated with Me₃SiN₃. The reactions of the aminophosphine **1** with elemental sulfur, MeI, and Me₃SiN₃ afforded the expected four-coordinate oxidation products (Me₃Si)₂NP(S)Me₂, **2**, [(Me₃Si)₂NPMe₃]⁺I⁻, **3**, and (Me₃Si)₂NP-(NSiMe₃)Me₂, **4**. When **1** was allowed to react with molecular oxygen, however, only the rearranged product, Me₃SiOP(NSiMe₃)Me₂, **5**, was obtained. Carbon-13 as well as ¹H NMR data are reported for compounds **1–5**.

Introduction

The chemistry and stereochemistry of compounds containing the bis(trimethylsilyl)amino substituent are often markedly different from that of the analogous dialkylamino derivatives. The steric bulk of the (Me₃Si)₂N group and its planar geometry at nitrogen[1] are responsible, in part, for such observations as the stability of unusually low coordination numbers and valence states,[2] high element–nitrogen rotational barriers,[3] and unexpected ground-state structures[4] in many bis(trimethylsilyl)amino-substituted compounds. Moreover, the chemistry of such compounds is sometimes reflective of the lability of the N-trimethylsilyl substituent toward intramolecular rearrangements.[5]

As part of a continuing investigation of silicon–nitrogen–phosphorus systems, this paper reports the synthesis and some derivative chemistry of [bis(trimethylsilyl)amino]dimethylphosphine, (Me₃Si)₂NPMe₂ (**1**). The primary aim of this study was to assess the effect of a bis(trimethylsilyl)amino substituent on the course of some common oxidative addition reactions of trivalent phosphorus, with particular interest directed toward possible silyl group migrations in the resulting products.

Results and Discussion

When chlorodimethylphosphine was allowed to react with the N-lithium derivative of bis(trimethylsilyl)amine in ether solution (eq 1), [bis(trimethylsilyl)amino]dimethylphosphine
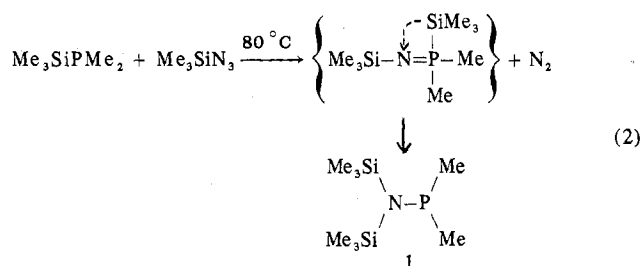
$$(Me_3Si)_2NLi + ClPMe_2 \rightarrow (Me_3Si)_2NPMe_2 + LiCl \qquad (1)$$
$$\mathbf{1}$$
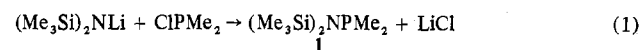
(**1**) was obtained.

A similar procedure has been used previously[6] for the synthesis of compound **1**; however, only low yields of an impure, poorly characterized product were reported. In the present study, compound **1**, a colorless, air-sensitive (see below) liquid, was routinely obtained in 60–70% yields and was readily purified by fractional distillation. It was fully characterized by NMR (¹H and ¹³C), infrared, and mass spectroscopy as well as elemental analysis.
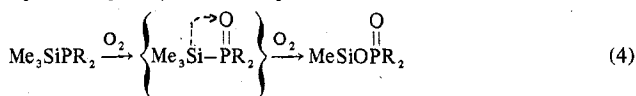
Unlike many similar reactions,[7,8] the preparation of compound **1** was found to be extremely sensitive to changes in reaction conditions. High yields of the product were obtained only when a dilute ether solution of Me₂PCl was added slowly to a vigorously stirred solution of LiN(SiMe₃)₂ at 0 °C.

Procedures similar to those used for the synthesis of other silylaminophosphines[8] such as the addition of Me₂PCl to LiN(SiMe₃)₂ at −78 °C, followed by slow warming to room temperature, gave substantially lower yields (<20%).

Somewhat surprisingly, the silylaminophosphine **1** was also isolated in a high yield from the reaction (eq 2) of (tri-

$$Me_3SiPMe_2 + Me_3SiN_3 \xrightarrow{80\,^\circ C} \left\{ \begin{array}{c} {-SiMe_3} \\ Me_3Si-N=P-Me \\ Me \end{array} \right\} + N_2$$

(2)

methylsilyl)dimethylphosphine with trimethylsilyl azide. This process can be viewed as a combination of two known reactions: the Staudinger phosphinimine synthesis[9] (eq 3) followed by migration of the Me₃Si group as occurs during the oxidation of silylphosphines[10] (eq 4).

$$R_3P + R'N_3 \rightarrow R_3P=NR' + N_2 \qquad (3)$$

$$Me_3SiPR_2 \xrightarrow{O_2} \left\{ Me_3Si-\overset{\overset{\rightarrow O}{|}}{\underset{\|}{P}}R_2 \right\} \xrightarrow{O_2} MeSiOPR_2 \qquad (4)$$

The success of this novel synthetic route (eq 2) to silylaminophosphines prompted us to attempt a similar reaction with Me₃SiPH₂ as a possible preparation of (Me₃Si)₂NPH₂, a compound not accessible by other methods. When Me₃SiPH₂ and Me₃SiN₃ were heated together in a sealed tube, no reaction occurred below 180 °C, and further heating gave only N₂, Me₃SiH, and unidentified yellow solids. These observations are consistent with the reduced basicity of the primary phosphine Me₃SiPH₂ relative to Me₃SiPMe₂ and the expected thermal instability of the silylaminophosphine (Me₃Si)₂NPH₂.

With the exception of its reaction with molecular oxygen, the derivative chemistry of the silylaminophosphine **1** was found to be similar to that of other trivalent phosphorus compounds. Thus, the reactions (eq 5–7) with sulfur, iodomethane, and trimethylsilyl azide proceeded rapidly under mild