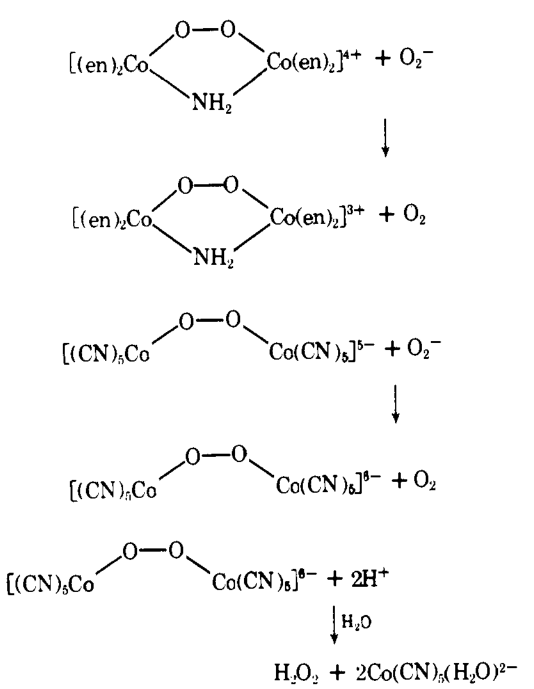
Scheme I



$8.86 \pm 0.43 \times 10^7$ M^{-1} s^{-1} is known.[18] It appears that the coordination of the superoxide with cobalt(III) has the same effect as the hydrogen ion in the superoxide dismutation reaction.

For the cyanide complex II we could not measure a rate constant with $O_2^-\cdot$ since the reaction is too slow to compete with the decay of $O_2^-\cdot$ by other processes. $HO_2\cdot$ reacts with the complex with a bimolecular rate constant of $4.7 \pm 0.3 \times 10^5$ M^{-1} s^{-1}. It appears that the rate with a negatively charged species like $O_2^-\cdot$ is drastically reduced for the cyanide complex due to electrostatic effects. This behavior is clearly indicated for the reduction processes of these complexes with unstable metal ions and free radicals.[19]

Superoxide ion reduction of metal ions like Cu(II) and Mn(III) complexes are known.[3-5,20-22] This is the first report of a reaction of superoxide ion with the bound superoxide other than hydroperoxide ion. The present investigation shows the existence of a pathway catalyzed by a transition-metal complex. Although no known superoxide dismutase contains cobalt, the present study emphasizes that in enzymatic mechanisms superoxo coordinated metal ion centers could exist and oxidize the superoxide ion analogously to the proton-catalyzed dismutation reaction.

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Palladium(II)-Promoted Cyclizations of Olefinic Silyl Enol Ethers. Preparations of σ-(1-Substituted 3-oxocyclopentyl)methylpalladium(II) Complexes and Their Oxidative Rearrangements

Sir:

In a preceding paper,[1] we reported that cyclization of 2-trimethylsilyloxy-1,5-hexadiene (**1a**) was performed by a catalyst of $Pd^{II}(OAc)_2$ in acetonitrile to produce 3-methyl-2-cyclopentenone (**5**). The Pd(II)-promoted cyclization of **1a** was explained by assuming an intermediate of oxo-π-allylpalladium(II) complex (**2a**), which undergoes intramolecular olefin insertion followed by β elimination of palladium hydride from the resultant σ-(3-oxocyclopentyl)methylpalladium(II) complex (**4a**) as shown in Scheme I. Herein, we report preparations of air-stable σ-(1-substituted 3-oxocyclopentyl)methylpalladium(II) chloride (acetonitrile) complexes (**4**) by Pd(II)-promoted cyclizations of 2-trimethylsilyloxy(5-substituted)-1,5-hexadienes (**1**) (Scheme I), and their oxidations with cupric chloride causing novel ring-expansion reactions (Scheme I).

A sample procedure for the preparation of σ-(1-substituted 3-oxocyclopentyl)methylpalladium(II) chloride (acetonitrile) complexes (**4**) is illustrated as follows. To a solution of $Pd^{II}Cl_2(PhCN)_2$ (1 mmol) in benzene (12 mL), silyl enol ether (**1d**, 1 mmol) was added and stirred at 8–10 °C for 2 h. The reaction mixture was condensed in vacuo to ca. one fourth of the volume and triturated with hexane (30 mL) to precipitate σ-(4-phenyl-4-pentenoyl)methylpalladium(II) chloride complex (**3d**,[2] 92%). Next, a solution of the palladium(II) complex (**3d**, 1 mmol) in acetonitrile (10 mL) was heated at reflux for 2 h. After the mixture was filtered to remove a small amount of depositing palladium metal, it was evaporated in vacuo to leave crude σ-(1-phenyl-3-oxocyclopentyl)methylpalladium(II) chloride (acetonitrile) complex (**4d**) in an 87% yield, which was recrystallized from acetonitrile to prepare an analytically pure sample.[3] Spectral data of **4d** [IR (KBr disk) 2305, 1735 cm^{-1}; NMR ($CDCl_3$ with Me_4Si) δ 1.98 (s, 3 H), 2.2–2.8 (m, 8 H), 7.1–7.7 (m, 5 H)] are consistent with the assigned structure. In support of the structure, hydrogenation of **4d** in benzene (1 atm of H_2, 1 h) furnished 3-methyl-3-phenylcyclopentanone (**6d**) quantitatively. The preparation of **4** can be more conveniently performed in one flask starting with olefinic silyl enol ether without the isolation of **3** just by changing the solvents. Similarly, olefinic silyl enol ethers **1b**, **1c**, **1e**, **1f**, and **1g** were cyclized to the corresponding complexes **4**[4] [**4b** (88%), **4c** (91%), **4e** (68%), **4f** (82%), and **4g** (96%)

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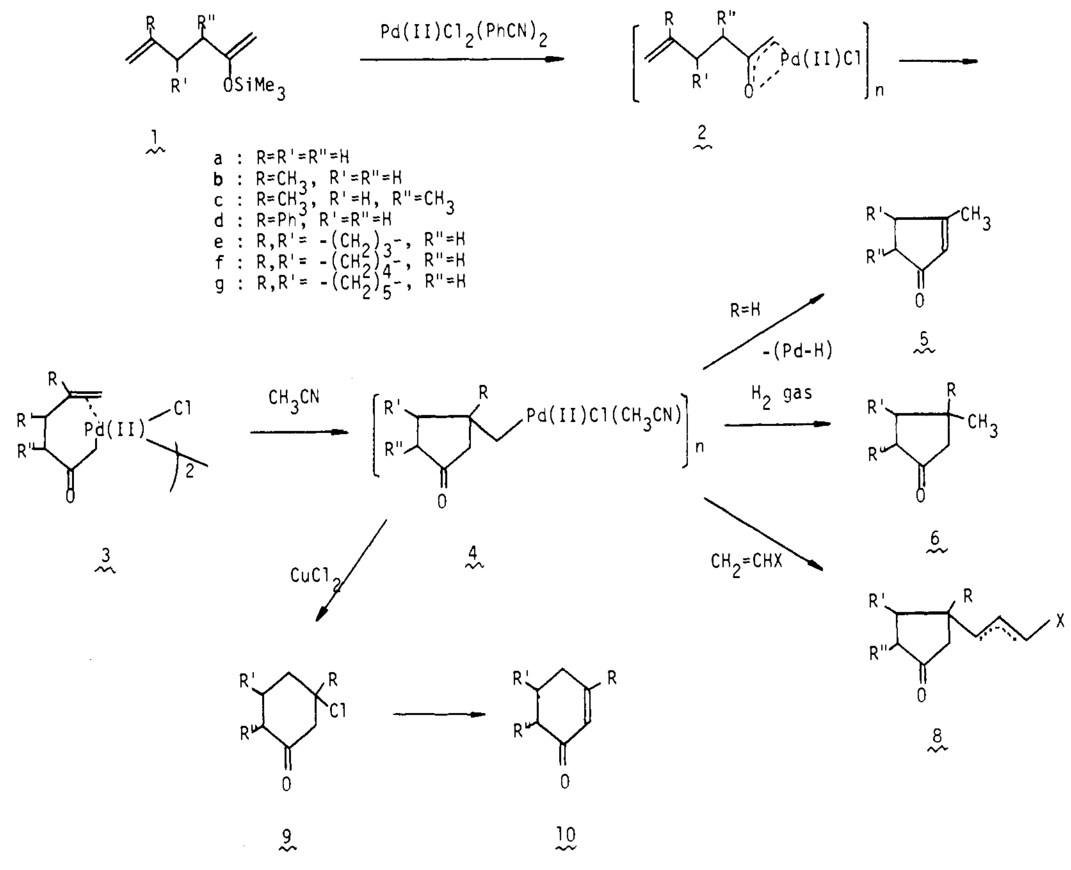
Scheme I



based upon the respective starting olefinic silyl enol ether (**1**)]. Hydrogenation of **4e**, **4f**, and **4g** presented a convenient synthesis of 1-methylbicyclo[*n*.3.0]alkanones (**6**). It is noteworthy that the new ring junction has almost exclusively cis stereochemistry (>98%) for **6e** and **6f** and trans stereochemistry (>90%) for **6g**. Identities of cis-fused 1-methylbicyclo[3.3.0]octan-3-one (**6e**) and cis-fused 1-methylbicyclo[4.3.0]nonan-8-one (**6f**) were established by comparison of their spectral data[5] with those of the respective authentic samples.[6,7] The structure of trans-fused 1-methylbicyclo[5.3.0]decan-9-one (**6g**) was assigned on the basis of elemental analysis[8] and IR and NMR spectra.[8] The trans stereochemistry of the ring junction in **6g** was determined by comparison[9] of its NMR spectrum (δ 0.94, methyl singlet) with that of cis-fused 1-methylbicyclo[5.3.0]decan-9-one (**6g'**) (δ 1.11, methyl singlet)[11] which was prepared by hydrogenation on Pd/C catalyst of 1-methylbicyclo[5.3.0]-7-decen-9-one (**7**).[12]

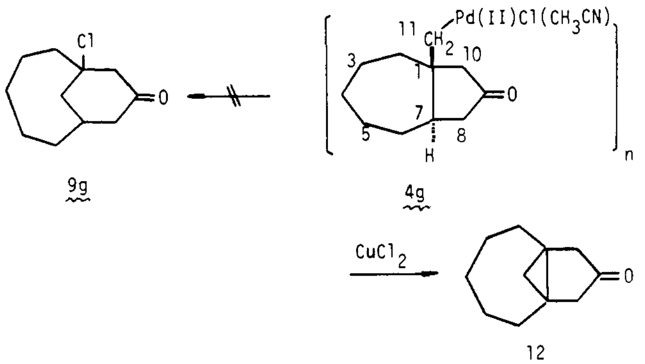
As was expected, complexes **4** reacted with olefins such as acrylate, methyl vinyl ketone, allyl chloride, and styrene by the addition-elimination mechanism to yield 3-alkyl- (or 3-aryl-) 3-alkenylcyclopentanones (**8**)[13] {**8b** (R = CH$_3$; R' = R'' = H, X = COCH$_3$) (86%); **8e** [R,R' = -(CH$_2$)$_3$-, R'' = H, X = COCH$_3$] (60%); **8f** [R,R' = -(CH$_2$)$_4$-, R'' = H, X = COCH$_3$] (53%); **8g** [R,R' = -(CH$_2$)$_5$-, R'' = H, X = CHO] (70%)}. 3-Substituted 3-(4-oxoalkenyl)cyclopentanones (**8b–g**) thus prepared can be utilized as synthetic intermediates for preparation of annelated cyclopentanones by the conventional methods.

Next, we describe a novel rearrangement of carbon skeleton induced by oxidative cleavage of the palladium–carbon bond of the complexes **4** with CuCl$_2$ (Scheme I). When palladium(II) complexes **4b** and **4c** were treated with cupric chloride, a novel ring expansion took place to afford 3-methyl-2-cyclohexenone (**10b**, 85%) and 3,6-dimethyl-2-cyclohexenone (**10c**, 82%), respectively.

The oxidative ring expansions of complexes **4** were performed according to the following procedure. To a solution of σ-(1-methyl-3-oxocyclopentyl)methylpalladium(II) chloride (acetonitrile) complex (**4b**) in acetonitrile, which had been prepared by heating a solution of 253 mg (1 mmol) of σ-(4-methyl-4-pentenoyl)methylpalladium(II) chloride (**3b**) in 10 mL of acetonitrile, a solution of 269 mg (2 mmol) of anhydrous cupric chloride in 3 mL of dimethylformamide was added at once at 0 °C with stirring. After the mixture was stirred for 3 h at room temperature, it was poured into aqueous NaHCO$_3$ and extracted with ether. The ether extract was evaporated and subjected to preparative GLC to afford 3-methyl-2-cyclohexenone (**10b**) in an 85% overall yield based upon **3b**. Similarly, the oxidation of **4c** with cupric chloride furnished 3,6-dimethyl-2-cyclohexenone (**10c**) in an 82% overall yield.

Successful extension of the oxidative ring-expansion technique to σ-1-(cis-fused bicyclo[*n*.3.0]alkanone)methylpalladium(II) complexes (**4e** and **4f**) has presented a new and novel synthesis of 1-chlorobicyclo[*n*.3.1]alkanones (**9e** and **9f**). On the similar treatment of σ-1-(cis-fused bicyclo[3.3.0]octan-3-one)methylpalladium(II) chloride (acetonitrile) complex (**4e**) with cupric chloride, 1-chlorobicyclo[3.3.1]nonan-3-one (**9e**) was produced in a 70% isolated yield, which was identified by comparison of its IR and NMR spectra with those reported by House.[14] The oxidative ring-expansion reaction of **4f** afforded, after the workup, crude 1-chlorobicyclo[4.3.1]decan-8-one (**9f**),[15] which on hydrogenation with Pd/C (1 atm of H$_2$, 10 h) gave bicyclo[4.3.1]decan-8-one (**11**)[16] in an 89% overall yield based on **3f**.

The oxidation of σ-1-(trans-fused bicyclo[5.3.0]decan-9-one)methylpalladium(II) chloride (acetonitrile) complex (**4g**) with cupric chloride was remarkably different from those of complexes **4e** and **4f**. When **4g** was treated with cupric chloride according to the procedure described, tricyclo[5.3.1.0]unde-



9g **4g** **12**

can-9-one (**12**) was produced in a 70% yield. The structure assignment of **12** is based upon elemental analysis and IR, ^{1}H NMR, and ^{13}C NMR spectra.[17] The structure is also consistent with a finding that **12** is treated with HCl in chloroform[18] to afford 1-methylbicyclo[5.3.0]-7-decen-9-one (**7**).[12]

At the present moment it is very difficult to explain the reason why the oxidation of σ-1-(trans-fused bicyclo[5.3.0]-decan-9-one)methylpalladium(II) complex (**4g**) takes a different reaction course from that of σ-1-(cis-fused bicyclo[n.3.0]alkanone)methylpalladium(II) complexes (**4e** and **4f**). Consideration with CPK molecular model suggests that the 1,2 shift of carbon bond C_7–C_1 to carbon bond C_7–C_{11} in the oxidative cleavage of the palladium carbon bond of **4g** leading to the expected 1-chlorobicyclo[5.3.1]undecan-9-one (**9g**) is susceptible to severe steric hindrance owing to the bond C_7–H. A detailed understanding of the reaction mechanism[19,20] must await further study.

Acknowledgment. We are indebted to Dr. T. Hiyama, Kyoto University, for ^{13}C NMR measurements. We are grateful to Shin-etsu Chemical Industry Co., Ltd., for providing the trimethylsilyl chloride.

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(2) **3d**: IR (KBr disk) 1655, 1565 cm^{-1}; NMR (CD$_3$CN with Me$_4$Si) δ 1.8–2.8 (m, 6 H), 4.23 (br s, 1 H), 4.89 (s, 1 H), 6.8–7.5 (m, 5 H); mol wt (vapor pressure osmometry in CHCl$_3$) calcd for dimer 630, found 647. Anal. Calcd for C$_{12}$H$_{13}$ClOPd: C, 45.74; H, 4.16; Cl, 11.25. Found: C, 45.79; H, 4.41; Cl, 11.02. Hydrogenation of **3d** gave 5-phenyl-2-hexanone in a quantitative yield. **3e**: IR (KBr disk) 1655, 1512 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.25–3.00 (m, 11 H), 4.39 (br s, 1 H), 4.60 (br s, 1 H). **3f**: IR (KBr disk) 1656, 1563, 1517 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.34–3.10 (m, 13 H), 4.05 (s, 1 H), 4.48 (s, 1 H). **3g**: IR (KBr disk) 1655, 1555, 1518 cm^{-1}.

(3) Anal. Calcd for C$_{14}$H$_{16}$ClNOPd (**4d**): C, 47.21; H, 4.53; Cl, 9.96; N, 3.93. Found: C, 47.29; H, 4.76; Cl, 9.74; N, 3.83.

(4) **4e**: IR (KBr disk) 2320, 2260, 1725 cm^{-1}. **4f**: IR (KBr disk) 2308, 2290, 1725 cm^{-1}. **4g**: IR (KBr disk) 2307, 2280, 1735 cm^{-1}.

(5) **6e**: IR (neat) 1743, 1450, 1404 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.15 (s, 3 H), 1.38–2.45 (m, 11 H).[8] **6f**: IR (neat) 1743, 1455, 1444 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.13 (s, 3 H), 1.18–2.45 (m, 13 H).[7] 2,4-Dinitrophenylhydrazone of **6f**: mp 142–145 °C.[7]

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(8) **6g**: IR (neat) 1745, 1450, 1405 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 0.94 (s, 3 H), 1.15–2.75 (m, 15 H). Anal. Calcd for C$_{11}$H$_{18}$O: C, 79.46; H, 10.92. Found: C, 79.68; H, 11.03.

(9) NMR signals of methyl groups of *trans*-1-methylbicyclo[3.3.0]octan-3-one (**6e'**)[6] and *trans*-1-methylbicyclo[5.3.0]decan-10-one[10] are more shielded than those of the respective cis isomers.

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(11) **6g'**: IR (neat) 1743, 1455, 1403 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.11 (s, 3 H), 1.16–2.20 (m, 13 H), 2.35–2.89 (m, 2 H).

(12) Karliner, J.; Budzikiewics, H.; Djerassi, C. *J. Am. Chem. Soc.* **1965**, *87*, 580. **7**: IR (neat) 3040, 1690, 1609, 1445 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.00–2.88 (m, 10 H), 1.18 (s, 3 H), 2.23 (s, 2 H), 5.69 (s, 1 H).

(13) For instance, σ-1-(cis-fused bicyclo[4.3.0]nonan-8-one)methylpalladium(II) chloride (acetonitrile) complex (**4f**, 1 mmol) was reacted with methyl vinyl ketone (3 mmol) in 10 mL of benzene at room temperature for 12 h to produce a mixture of cis-fused 1-(*trans*-4-oxo-1-pentenyl)bicyclo[4.3.0]-nonan-8-one (**8f-I**, 21%) and cis-fused 1-(*trans*-4-oxo-2-pentenyl)bicyclo[4.3.0]nonan-8-one (**8f-II**, 32%). **8f-I**: IR (neat) 1740, 1710, 978 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.11–2.68 (m, 13 H), 2.13 (s, 3 H), 3.14 (m, 2 H), 5.58 (m, 2 H). **8f-II**: IR (neat) 1735, 1668, 1623, 980 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.11–2.75 (m, 15 H), 2.18 (s, 3 H), 5.58–6.21 (m, 1 H), 6.36–7.03 (m, 1 H).

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(15) Attempts to prepare an analytically pure sample of **9f** failed, because it partially decomposed during column chromatography and thin layer chromatography on silica gel and alumina. **9f**: IR (neat) 1710 cm^{-1}; ^{1}H NMR (CDCl$_3$ with Me$_4$Si) δ 1.05–2.75 (m, 13 H), 2.86 (s, 2 H); mass M$^+$ 188 and 186 (1:3).

(16) **11**: mp 53–55 °C; IR (Nujol) 1705 cm^{-1}; ^{13}C NMR (CDCl$_3$ with Me$_4$Si) δ 26.03, 31.30, 34.74, 35.19, 48.49, 207.08.

(17) **12**: IR (neat) 3030, 1745 cm^{-1}; ^{1}H NMR (CDCl$_3$ with Me$_4$Si) δ 0.31 (d, 1 H), 0.85 (m, 1 H), 1.08–2.83 (m, 14 H); ^{13}C NMR (CDCl$_3$ with Me$_4$Si) δ 25.28, 26.56, 28.43, 32.05, 33.29, 46.75, 216.80. Anal. Calcd for C$_{11}$H$_{16}$O: C, 80.44; H, 9.83. Found: C, 80.68; H, 10.10.

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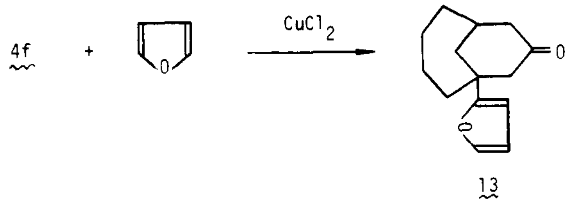
(19) On treatment of **4f** with cupric chloride in the presence of furan, 1-(2-furyl)bicyclo[4.3.1]decan-8-one (**13**) was produced in a 30% isolated yield based on **3f**. **13**: IR (neat) 3100, 1710 cm^{-1}; NMR (CDCl$_3$ with Me$_4$Si) δ 1.31–2.89 (m, 15 H), 5.96 (m, 1 H), 6.25 (m, 1 H), 7.31 (m, 1 H). This finding may be taken to suggest that carbonium-ion intermediate is generated in the present oxidative cleavage of palladium–carbon bond of palladium(II) complexes (**4**).



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Structure and Bonding in a Phosphenium Ion–Metal Complex, $\mathrm{CH_3\overline{NCH_2CH_2N(CH_3)}PMo(\eta^5\text{-}C_5H_5)(CO)_2}$. An Example of a Molybdenum–Phosphorus Multiple Bond

Sir:

Heterolytic cleavage of the phosphorus–halogen bond in aminohalophosphines, induced by halide ion acceptors, has been shown to result in the formation of novel dicoordinate aminophosphenium ions, $(R_2N)_2P^+$.[1-6] The molecular structure of only one aminophosphenium ion has been determined,[6] and the bonding and coordination chemistry displayed by these cations have not been extensively explored.[7] We have previously reported the synthesis of several neutral metallophosphenium ion coordination complexes;[10] however, the molecular structures of these complexes have not been unambiguously determined, and the nature of the metal atom–phosphorus cation interaction is open to question.[9,11-13] We report here the determination of the exact composition and molecular structure of a neutral metallophosphenium ion complex (**1**), isolated from the reaction of $\mathrm{CH_3\overline{NCH_2CH_2N(CH_3)}PF}$ (**2**) with $\mathrm{Na(\eta^5\text{-}C_5H_5)Mo(CO)_3}$. An informative description of the bonding in **1** is also provided by quantitative molecular orbital calculations.

Compound **1** was prepared as described previously[11,14] except that the addition of the ligand **2** to the THF solution of NaCpMo(CO)$_3$ was accomplished in vacuo. Carbon monoxide was evolved and quantitatively recovered with a Toepler pump system. The amount of CO produced is consistent with a reaction summarized by the following equation:

$$\underset{\mathbf{2}}{\mathrm{CH_3\overline{NCH_2CH_2N(CH_3)}PF}} + \mathrm{NaCpMo(CO)_3} \xrightarrow{\text{THF}} \underset{\mathbf{1}}{\mathrm{CH_3\overline{NCH_2CH_2N(CH_3)}PMoCp(CO)_2}} + \mathrm{CO} + \mathrm{NaF}$$

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