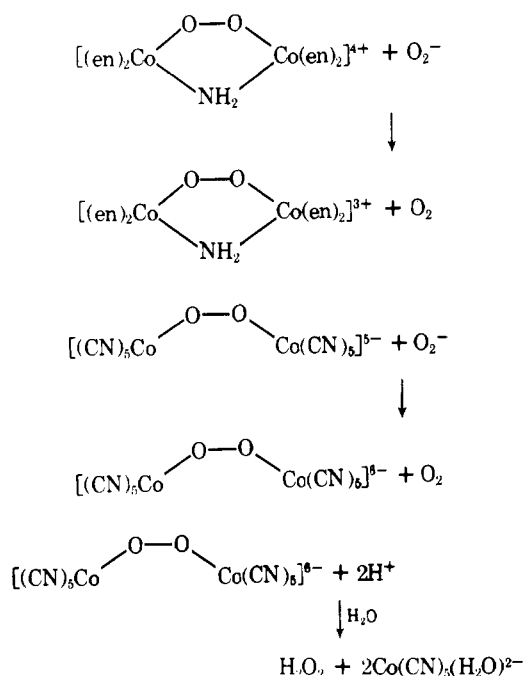


Scheme I



$8.86 \pm 0.43 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ 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^- since the reaction is too slow to compete with the decay of O_2^- by other processes. HO_2^- reacts with the complex with a bimolecular rate constant of $4.7 \pm 0.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. It appears that the rate with a negatively charged species like O_2^- 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.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2101 from the Notre Dame Radiation Laboratory.

References and Notes

- (1) J. A. Fee and G. J. McClune in "Mechanisms of Oxidising Enzymes", T. P. Singer and R. N. Oudar, Eds., Elsevier, North Holland, 1978.
- (2) J. Wilshire and D. T. Sawyer, *Acc. Chem. Res.*, **12**, 105 (1979).
- (3) A. M. Michelson, J. M. McCord, and I. Fridovich, Eds., "Superoxide and Superoxide Dismutases", Academic Press, London, 1977.
- (4) J. S. Valentine and A. Quinn, *Inorg. Chem.*, **15**, 1997 (1976).
- (5) G. J. McClune, J. A. Fee, G. A. McCluskey, and J. T. Groves, *J. Am. Chem. Soc.*, **99**, 5220 (1977).
- (6) A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, **13**, 1 (1970).
- (7) W. P. Schafer and R. W. Marsh, *Acta Crystallogr.*, **21**, 735 (1960).
- (8) (a) A. G. Sykes, *Chem. Br.*, **10**, 170 (1974). (b) For the preparations and reactions of the complexes, see *Inorg. Synth.*, **12**, 197 (1972).
- (9) R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, **79**, 139 (1979).
- (10) K. Chandrasekaran and P. Natarajan, *J. Chem. Soc., Chem. Commun.*, 774 (1977).
- (11) P. Natarajan and N. V. Raghavan, *J. Chem. Soc., Chem. Commun.*, 268 (1980).

- (12) K. Chandrasekaran and P. Natarajan, *Inorg. Chem.*, **19**, 1714 (1980).
- (13) J. Rabani, D. Klugroth, and J. Lilie, *J. Phys. Chem.*, **77**, 1169 (1973).
- (14) L. K. Patterson and J. Lilie, *Int. J. Radiat. Phys. Chem.*, **6**, 129 (1974).
- (15) P. Natarajan and N. V. Raghavan, manuscript in preparation.
- (16) A. Haim and W. K. Wilmarth, *J. Am. Chem. Soc.*, **83**, 509 (1961).
- (17) D. Behar, G. Czapski, L. M. Dorfman, J. Rabani, and H. A. Schwarz, *J. Phys. Chem.*, **74**, 3209 (1970).
- (18) B. H. J. Bielski and A. O. Allen, *J. Phys. Chem.*, **81**, 1048 (1977).
- (19) The bimolecular rate constants for the reduction by CO_2^- ion are 5.7×10^9 and $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for I and II, respectively.¹⁵
- (20) J. K. Howie, and D. T. Sawyer, *J. Am. Chem. Soc.*, **98**, 6698 (1976).
- (21) J. Stein, J. P. Fackler, G. J. McClune, J. A. Fee, and L. T. Chan, *Inorg. Chem.*, **18**, 3511 (1979).
- (22) J. S. Valentine and A. B. Curtis, *J. Am. Chem. Soc.*, **97**, 224 (1975).
- (23) (a) University of Notre Dame; (b) University of Madras; (c) address correspondence to the University of Notre Dame.

P. Natarajan,*²³ N. V. Raghavan^{23a}

Radiation Laboratory, University of Notre Dame
Notre Dame, Indiana 46556, and
Department of Chemistry, University of Madras,
Tiruchirapalli 620020, India
Received February 25, 1980

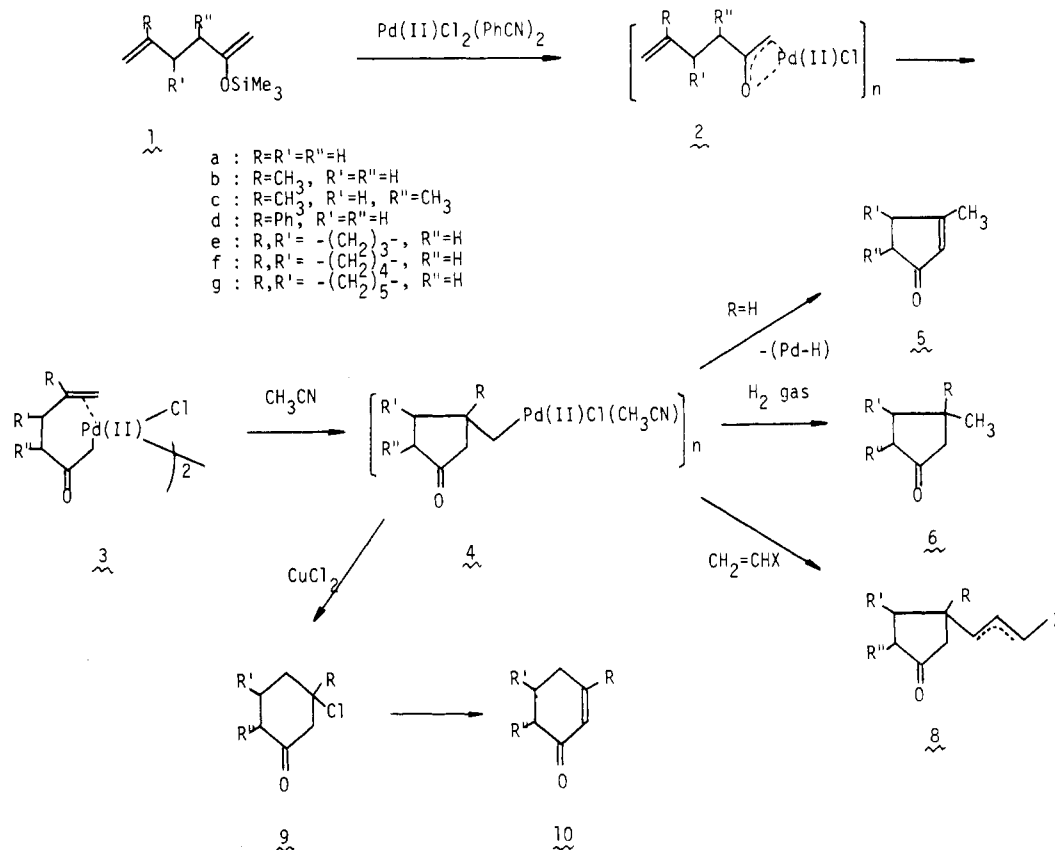
Palladium(II)-Promoted Cyclizations of Olefinic Silyl Enol Ethers. Preparations of σ -(1-Substituted 3-oxocyclopentyl)methylpalladium(II) Complexes and Their Oxidative Rearrangements

Sir:

In a preceding paper,¹ we reported that cyclization of 2-trimethylsilyloxy-1,5-hexadiene (**1a**) was performed by a catalyst of $\text{Pd}^{\text{II}}(\text{OAc})_2$ 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 -allyl-palladium(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 $\text{Pd}^{\text{II}}\text{Cl}_2(\text{PhCN})_2$ (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-pentenyl)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%)

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 data⁵ 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 analysis⁸ and IR and NMR spectra.⁸ The *trans* stereochemistry of the ring junction in **6g** was determined by comparison⁹ 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

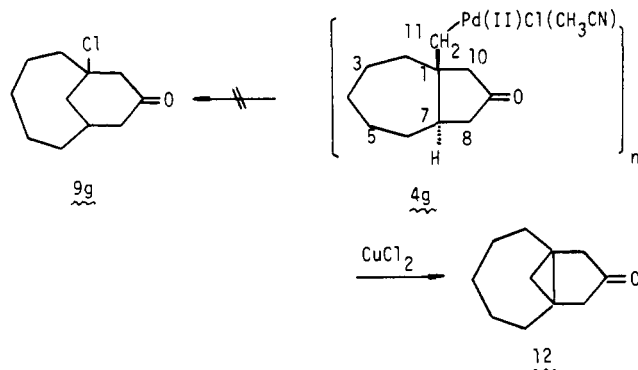
As was expected, complexes **4** reacted with olefins such as acrylate, methyl vinyl ketone, allyl chloride, and styrene by the addition-elimination mechanism to yield 3-alkyl- (or 3-aryl-) 3-alkenylcyclopentanones (**8**)¹³ {**8b** (R = CH₃; R' = R'' = H, X = COCH₃) (86%); **8e** [R, R' = -(CH₂)₃-, R'' = H, X = COCH₃] (60%); **8f** [R, R' = -(CH₂)₄-, R'' = H, X = COCH₃] (53%); **8g** [R, R' = -(CH₂)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 CuCl₂ (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-pentenyl)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 NaHCO₃ 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 H₂, 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-



can-9-one (**12**) was produced in a 70% yield. The structure assignment of **12** is based upon elemental analysis and IR, ^1H NMR, and ^{13}C NMR spectra.¹⁷ The structure is also consistent with a finding that **12** is treated with HCl in chloroform¹⁸ to afford 1-methylbicyclo[5.3.0]-7-decen-9-one (**7**).¹²

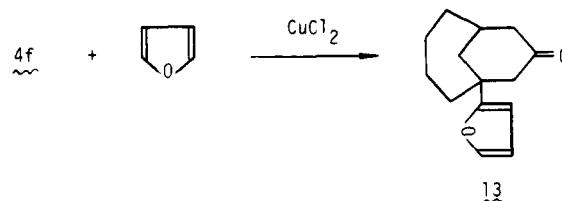
At the present moment it is very difficult to explain the reason why the oxidation of σ -1-(trans-fused bicyclo[5.3.0]-decan-9-one)methylpalladium(II) complex (**4g**) takes a different reaction course from that of σ -1-(cis-fused bicyclo[n .3.0]alkanone)methylpalladium(II) complexes (**4e** and **4f**). Consideration with CPK molecular model suggests that the 1,2 shift of carbon bond $\text{C}_7\text{--C}_1$ to carbon bond $\text{C}_7\text{--C}_{11}$ 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 $\text{C}_7\text{--H}$. 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.

References and Notes

- Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494.
- 3d**: IR (KBr disk) 1655, 1565 cm^{-1} ; NMR (CD_3CN with Me_4Si) 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 $\text{C}_{12}\text{H}_{12}\text{ClO}_2\text{Pd}$: 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_4Si) 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_4Si) 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} .
- Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{INO}_2\text{Pd}$ (**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.
- 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} .
- 6e**: IR (neat) 1743, 1450, 1404 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.15 (s, 3 H), 1.38–2.45 (m, 11 H). **6f**: IR (neat) 1743, 1455, 1444 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.13 (s, 3 H), 1.18–2.45 (m, 13 H). **7**: 2,4-Dinitrophenylhydrazone of **6f**: mp 142–145 $^\circ\text{C}$.
- Granger, R.; Vidal, J. P.; Girard, J. P.; Chapat, J. P. *C. R. Acad. Sci., Ser. C* **1970**, *270*, 2022.
- Ratchliffe, B. E.; Heathcock, C. H. *J. Org. Chem.* **1972**, *37*, 531.
- 6g**: IR (neat) 1745, 1450, 1405 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 0.94 (s, 3 H), 1.15–2.75 (m, 15 H). Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}$: C, 79.46; H, 10.92. Found: C, 79.68; H, 11.03.
- NMR signals of methyl groups of *trans*-1-methylbicyclo[3.3.0]octan-3-one (**6e**)⁹ and *trans*-1-methylbicyclo[5.3.0]decan-10-one¹⁰ are more shielded than those of the respective *cis* isomers.
- Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 290.
- 6g**: IR (neat) 1743, 1455, 1403 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.11 (s, 3 H), 1.16–2.20 (m, 13 H), 2.35–2.89 (m, 2 H).
- Karliner, J.; Budzikiewicz, H.; Djerassi, C. *J. Am. Chem. Soc.* **1965**, *87*, 580. **7**: IR (neat) 3040, 1690, 1609, 1445 cm^{-1} ; NMR (CDCl_3 with Me_4Si) δ 1.00–2.88 (m, 10 H), 1.18 (s, 3 H), 2.23 (s, 2 H), 5.69 (s, 1 H).
- 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_4Si) 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_4Si) 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).

- House, H. O.; Kleschick, W. A.; Zaiko, E. J. *J. Org. Chem.* **1978**, *43*, 3653.
- 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} ; ^1H NMR (CDCl_3 with Me_4Si) δ 1.05–2.75 (m, 13 H), 2.86 (s, 2 H); mass M^+ 188 and 186 (1:3).
- 11**: mp 53–55 $^\circ\text{C}$; IR (Nujol) 1705 cm^{-1} ; ^{13}C NMR (CDCl_3 with Me_4Si) δ 26.03, 31.30, 34.74, 35.19, 48.49, 207.08.
- 12**: IR (neat) 3030, 1745 cm^{-1} ; ^1H NMR (CDCl_3 with Me_4Si) 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_4Si) δ 25.28, 26.56, 28.43, 32.05, 33.29, 46.75, 216.80. Anal. Calcd for $\text{C}_{11}\text{H}_{16}\text{O}$: C, 80.44; H, 9.83. Found: C, 80.68; H, 10.10.
- Birch, A. J.; Subba Rao, G. S. R. *J. Chem. Soc.* **1965**, 5139.
- 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_4Si) 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**).
- (a) Boontanonda, P.; Grigg, R. *J. Chem. Soc., Chem. Commun.* **1977**, 583. (b) Backvall, J.-E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 393.

Yoshihiko Ito, Hirokazu Aoyama, Takeo Saegusa*

Department of Synthetic Chemistry
Faculty of Engineering, Kyoto University
Kyoto 606, Japan

Received December 4, 1979

Structure and Bonding in a Phosphenium Ion–Metal Complex, $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PMo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$. 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, $(\text{R}_2\text{N})_2\text{P}^+$.^{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 $\text{CH}_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{PF}$ (**2**) with $\text{Na}(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3$. 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 $\text{NaCpMo}(\text{CO})_3$ 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:

