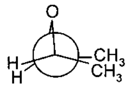
Eliminative Ring Opening of Oxiranium Ions in the Gas Phase[**]

Gabriele Renzi, Graziella Roselli, Felice Grandinetti, Antonello Filippi, and Maurizio Speranza*

When a base interacts with a substrate containing a nucleofuge,[1] two competing reactions generally take place: 1,2-elimination and nucleophilic substitution.[2] Exceptions to this dual behavior are rare in solution.[3] One such exception concerns the ring opening of three-membered heterocycles in acidic solutions, which normally proceeds by nucleophilic displacement and not by 1,2-elimination.[4] This is due to the pronounced s character of the carbon atoms of the three-membered ring, which minimizes repulsive nonbonding interactions in the substitution transition structure (TS).[5] Eliminative ring cleavage becomes observable to a limited extent in three-membered cycles only when the competing substitution is sterically inhibited, as in the reaction between *cis*-1,1,2,3-tetramethylaziridinium ions and *N*-ethyldiisopropylamine (Hünig's base).[5a,b, 6] The bulky Hünig's base interacts only with the exocyclic hydrogen atoms of the encumbered solvated ion,[6] so that small amounts of the corresponding Hoffmann olefin, *N*,*N*-dimethyl-3-aminobut-1-ene, are exclusively formed. No examples of eliminative ring cleavage of three-membered heterocycles following the Saytzeff rule have been presented to date.

Here we provide the first experimental evidence for the occurrence of this unprecedented elimination reaction in the gas phase.[7] The reaction is induced by the attack of a powerful base, $N(CH_3)_3$, on the ions **Is**/**Ia** and **II**. Epimers *cis*-**Is**/**Ia** and the *trans* isomer **II**[8] are generated in the gas phase by methylation of *cis*- (**1**) and *trans*-2,3-butene oxide (**2**) with $(CH_3)_2F^+$ ions,[9] which are formed in known yields by γ-radiolysis of CH_3F (760 torr, ^{60}Co source). If not rapidly neutralized by collision with a gaseous base, ions **Is**/**Ia** and **II** tend to rearrange exclusively to the more stable open-chain isomer **III**, which eventually neutralizes to ketone **3** (Scheme 1).[9, 10]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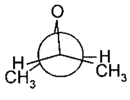
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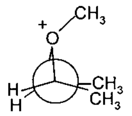
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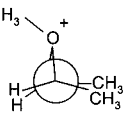
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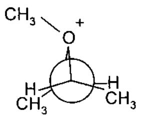
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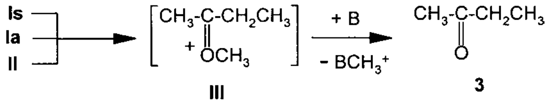


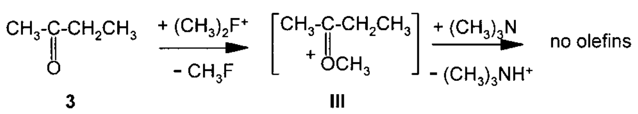
Scheme 1. B = base.

In the presence of $N(CH_3)_3$ (proton affinity (PA) = 226.8 kcal mol^{-1}),[11] **3** is formed along with appreciable amounts of the *E* and *Z* isomers of 2-methoxy-2-butene (**4E** and **4Z**, see Scheme 3; Table 1).[12] No production of 3-methoxy-1-butene is observed. Formation of alkenes **4E** and **4Z** requires the presence of both **Is**/**Ia** (or **II**) and $N(CH_3)_3$. In fact, no olefins are recovered: 1) in the gaseous mixtures if they are not submitted to irradiation; 2) in the irradiated mixtures if $N(CH_3)_3$ is replaced by the milder base NH_3 (PA(NH_3) = 204.0 kcal mol^{-1});[11] and 3) in the irradiated mixtures if the **Is**/**Ia** or **II** intermediates are replaced by ion **III**, which is directly formed in the same medium upon methylation of **3** by $(CH_3)_2F^+$ (Scheme 2).

Table 1. Yields of the products from the gas-phase attack of $(CH_3)_3N$ on **Is**/**Ia** and **II**, formed by O-methylation of **1** and **2** (see Schemes 1 and 3).[a]

Amount [torr]		T [°C]	Yields [%]			**4E**:**4Z**	$G_{(M)}$[b]
Substrate	$(CH_3)_3N$		**4E**	**4Z**	**3**		
1, 1.61	1.64	37	19.0	6.2	74.8	3.07	0.24
1, 1.49	1.54	60	21.4	4.2	74.4	5.07	0.31
1, 1.53	1.59	80	25.9	2.0	69.2	12.80	0.49
1, 1.58	1.62	100	28.3	1.0	70.7	27.60	0.49
2, 1.47	1.53	37	14.9	6.4	78.7	2.31	0.25
2, 1.53	1.61	60	17.2	5.8	77.0	3.00	0.33
2, 1.57	1.64	80	25.0	5.8	69.2	4.28	0.43
2, 1.46	1.52	100	26.7	5.1	68.2	5.27	0.43

[a] Bulk gas: 760 torr CH_3F, 10 torr O_2. Radiation dose 2×10^4 Gy (dose rate 1×10^4 Gy h^{-1}). [b] Absolute yields of products, expressed as their $G_{(M)}$ values (the number of molecules M produced per 100 eV of energy absorbed by the gaseous mixture). Each value is the average of several determinations, with an uncertainty level of about 5%. The detection limit for $G_{(M)}$ is 2×10^{-3}.



Scheme 2.

The last point (3) excludes that olefins **4E** and **4Z** arise from deprotonation of **III**, which is an abundant intermediate in the irradiated systems of Table 1, by $N(CH_3)_3$. This is testified by the high yield of butanone **3**. On these grounds, olefins **4E** and **4Z** are thought to arise from exothermic eliminative ring opening (Scheme 3).[13]

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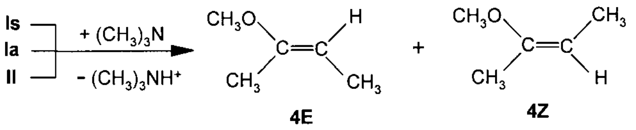

Scheme 3.

The exclusive recovery of the Saytzeff olefins **4E** and **4Z**, coupled with the absence of the Hoffmann isomer 3-methoxy-1-butene, indicate that in the gas phase $N(CH_3)_3$ abstracts selectively the most acidic ring protons of **Is**, **Ia**, and **II**. Irrespective of the structure of the starting epoxide, whether **1** or **2**, olefin **4E** invariably prevails over the more stable isomer **4Z**[14] to an extent which increases with reaction temperature (Table 1). This implies that the reaction in Scheme 3 is 1) kinetically controlled under all conditions and 2) governed by stereoelectronic factors, despite the quasi-orthogonality of the C_β–O and C_α–H bonds involved in the process.[15]

Quantum-chemical calculations at the B3LYP/6-31G* level of theory have been employed to gather information about the mechanism of the reaction in Scheme 3.[13] Since the molecular complexity of the species involved makes the accurate theoretical description of this reaction computationally unfeasible, we limited our analysis to a strictly related model reaction, that is, the NH_3-induced eliminative ring opening of O-methylated ethene oxide (**IV**) to yield NH_4^+ and methyl vinyl ether (**5**). The relevant free energy profile (298 K) is illustrated in Figure 1 along with the relevant isomer adducts and transition states. The reported energetics are not appreciably affected by upgrading the level of the calculation to B3LYP/6-31+G(d,p).

Ion **IV** interacts with ammonia to give two isomer adducts, **IVs** and **IVa**, which can interconvert either by O^+ epimerization through the **EP** TS or by backdissociation (Figure 1). Intrinsic reaction coordinate (IRC) calculations indicate that ring opening of **IVs** and **IVa** leads to complex **V** via the **SS** and **SA** (from **IVs**) and **AA** and **AS** TSs (from **IVa**). This process is characterized by extensive C_β–O bond cleavage, negligible C_αH proton transfer to ammonia, and partial rotation of the $C_\beta H_2^+$ moiety either clockwise (**AA** and **SA**) or counterclockwise (**SS** and **AS**). Evolution of these TSs to product **V** requires alignment of the empty orbital of the $C_\beta H_2^+$ rotor with the vicinal C_α–H bond prior of transfer of the proton to NH_3. Rotation may be assisted by the CH_3O lone pair, as in the paths involving **SA** and **AS**, or may not, as in those involving **SS** and **AA**. The lower energy levels of the **SA** and **AS** TSs are due to the orbital arrangement, which is reminiscent of that of the concerted *anti* and *syn* E2 eliminations. No similar orbital arrangements is present in the higher energy **SS** and **AA** TSs.

The above picture can be qualitatively extended to the more exothermic process shown in Scheme 3.[13] Interaction of $(CH_3)_3N$ with the ring hydrogen atoms of **II** is expected to generate the quasi-resonant *syn*-**IVs**^{t} and *anti*-**IVa**^{t} adducts.[8] Since the TSs for ring opening of these species involve the formation of the secondary $CH_3C_\beta H^+$ moiety, the magnitude of the relevant energy barriers is expected to be substantially lower than those reported in Figure 1. As a consequence, ring opening of **IVs**^{t} and **IVa**^{t} is allowed to compete with interconversion (**IVs**^{t} ↔ **IVa**^{t}).[16] Therefore, the **IVs**^{t} and **IVa**^{t} adducts are formed in comparable proportions, which are not

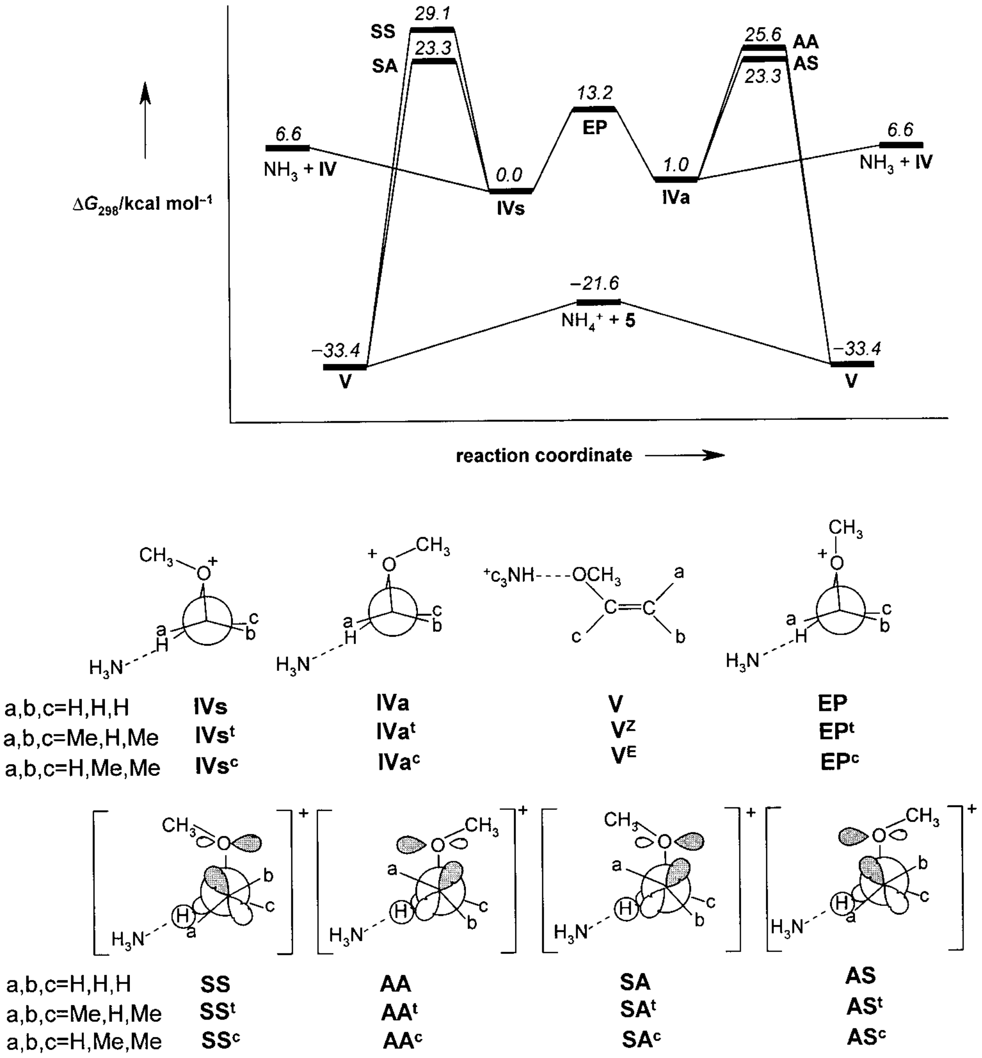

Figure 1. Top: Profile of the free energy (ΔG_{298}) of the NH_3-induced eliminative ring opening of O-methylated ethene oxide as calculated at the B3LYP/6-31G* level of theory. The relative energies are shown in italics. Bottom: Schematic representation of the isomer adducts and transition states involved.

significantly affected by temperature.[17] According to Figure 1, the ring opening of **IVs**^{t} and **IVa**^{t} should involve very similar free energies of activation corresponding to TSs **SA**^{t} and **AS**^{t}, respectively. Thus, a quasi-equimolar mixture of isomers of 2-methoxy-2-butene should be formed ($\mathbf{SA^t} \rightarrow \mathbf{V^Z} \rightarrow \mathbf{4Z} + \mathrm{HNMe_3^+}$; $\mathbf{AS^t} \rightarrow \mathbf{V^E} \rightarrow \mathbf{4E} + \mathrm{HNMe_3^+}$). As a matter of fact, formation of the **4E** isomer always predominates (Table 1). A plausible rationale for this lack of balance may be found in the presence of repulsive interactions in **SA**^{t} and **AA**^{t} between the OCH_3 group and the CH_3 moiety of the $CH_3C_\beta H^+$ rotor, which may increase the energy barriers corresponding to **SA**^{t} and **AA**^{t} relative to those of **SS**^{t} and **AS**^{t}. In fact, no similar repulsive interactions operate in these latter TSs.

A somewhat different picture arises for the attack of $(CH_3)_3N$ on the ring hydrogen atoms of **Is** and **Ia**. The attack gives rise to the *syn*-**IVs**^{c} and the *anti*-**IVa**^{c} adducts, which may interconvert only through the **EP**^{c} TS. Since the *syn*-**IVs**^{c} adduct is appreciably more stable than the *anti*-**IVa**^{c} adduct,[8] the relative population of the adducts leans more and more toward the *syn* complex as the reaction temperature increases.[17] If, as assumed above, repulsive interactions operate between the OCH_3 group and the CH_3 moiety of the $CH_3C_\beta H^+$ rotor, the energy barriers corresponding to **SS**^{c} and **AS**^{c} should increase relative to those of **SA**^{c} and **AA**^{c}. Thus, the energy difference between **SA**^{c} and **SS**^{c} should increase and that between **AA**^{c} and **AS**^{c} should decrease or even invert. As a result of the latter, ring opening of the *anti*-**IVa**^{c} adduct is expected to lead to comparable proportions of **4E** and **4Z** or even to predominance of **4E** over **4Z** ($\mathbf{AS^c} \rightarrow \mathbf{V^Z} \rightarrow \mathbf{4Z} + \mathrm{HNMe_3^+}$; $\mathbf{AA^c} \rightarrow \mathbf{V^E} \rightarrow \mathbf{4E} + \mathrm{HNMe_3^+}$). Instead, ring opening of the *syn*-**IVs**^{c} adduct would mostly lead to **4E** ($\mathbf{SA^c} \rightarrow \mathbf{V^E} \rightarrow \mathbf{4E} + \mathrm{HNMe_3^+}$). This may account for both the high selectivity of **4E** over **4Z** for the eliminative ring opening of **1**, as compared to that of **2**, and the pronounced positive temperature dependence of this selectivity (Table 1).[17]

In conclusion, it has been demonstrated that eliminative ring opening of oxiranium ions is a relatively facile process in the gas phase. The reaction involves preliminary ring opening of the charged moiety favored by interaction of its acidic protons with the base. A combination of stereoelectronic and conformational factors accounts for the high stereoselectivity of the reaction.

Experimental Section

Quantum-chemical calculations were performed using a IBM RISC/6000 version of the GAUSSIAN 94 set of programs.[18] The 6-31G* basis set was employed for all the atoms to optimize the geometries of the investigated species at the density functional level of theory, using the B3LYP functional which combines Becke's three-parameter hybrid description of exchange and the correlation functional of Lee, Yang, and Parr.[19] The total energies were refined by single-point calculations at the B3LYP/6-31+G(d,p) level of theory. The correspondence between the various transition structures and the energy minima of Figure 1 was ascertained by intrinsic reaction coordinate (IRC) calculations.[20]

The gaseous mixtures of Table 1 were prepared by conventional vacuum techniques.[9] The irradiation was carried out at constant temperature (37, 60, 80, and 100 °C) in a 220 Gammacell (Nuclear Canada Ltd.) to a total dose of 2×10^4 Gy at a rate of 1×10^4 Gy h^{-1}, as determined by a neopentane dosimeter. The irradiated mixtures were analyzed using a Hewlett-Packard 5890/II gas chromatograph equipped with a flame ionization detector. The following columns were employed: a) a 30-m (0.25 mm inner diameter) Vocol™ fused silica capillary column operated at 35–150 °C (4 °C min^{-1}); b) a 100-m (0.25 mm inner diameter) Petrocol™ fused silica capillary column operated at 35–200 °C (2 °C min^{-1}); c) a 30-m (0.32 mm inner diameter) Supelcowax fused silica capillary column operated at 50–230 °C (4 °C min^{-1}). The products were identified by coincidence of their retention volumes with those of authentic reference compounds, and their identity was confirmed by gas liquid chromatography/mass spectrometry with a Hewlett-Packard 5971A mass spectrometer. The yields were measured from the areas of the corresponding eluted peaks, using the internal standard calibration method.

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[1] C. J. M. Stirling, *Acc. Chem. Res.* **1979**, *12*, 198.

[2] a) F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry*, Plenum, New York, **1984**, Part A; b) T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry, 2nd ed.*, Harper and Row, New York, **1981**.

[3] See, for instance: R. J. Palmer, C. J. M. Stirling, *J. Chem. Soc. Chem. Commun.* **1978**, 338.

[4] a) J. G. Buchanan, H. Z. Sable in *Selective Organic Transformation*, *Vol. 1* (Ed.: B. S. Thygarajan), Wiley, New York, **1972**; b) R. E. Parker, N. S. Isaacs, *Chem. Rev.* **1959**, *59*, 737; c) A. Rosowsky in *Heterocyclic Compounds with Three- and Four-Membered Rings*, *Part 1* (Ed.: A. Weissberger), Interscience, New York, **1964**, pp. 1–523; d) J. A. Deyrup in *Small Ring Heterocycles*, *Vol. 42*, *Part 1* (Ed.: A. Hassner), Wiley, New York, **1983**, chap. 1.

[5] a) C. Lillocci, *J. Org. Chem.* **1988**, *53*, 1733; b) G. Gionta, C. Lillocci, *J. Phys. Org. Chem.* **1993**, *6*, 187; c) G. Frachey, G. Gionta, C. Lillocci, *Gazz. Chim. Ital.* **1993**, 463.

[6] The active role of the solvent (CH_3CN) in this reaction is testified by the predominant formation of 4,5-dihydro-1,1,2,4,5-pentamethylimidazolium ion as the substitution product.[5b]

[7] M. J. S. Dewar, Y. C. Yuan, *J. Am. Chem. Soc.* **1990**, *112*, 2088; M. J. S. Dewar, Y. C. Yuan, *J. Am. Chem. Soc.* **1990**, *112*, 2095.

[8] At the B3LYP/6-31G* level of theory: $\Delta G_{298}(\mathbf{Is}) - \Delta G_{298}(\mathbf{Ia}) = +3.4$ kcal mol^{-1}; $\Delta G_{298}(\mathbf{II}) - \Delta G_{298}(\mathbf{Ia}) = +0.6$ kcal mol^{-1}.

[9] a) G. Angelini, M. Speranza, *J. Chem. Soc. Chem. Commun.* **1978**, 213; b) M. Speranza, G. Angelini, *J. Am. Chem. Soc.* **1980**, *102*, 3115.

[10] In the absence of $N(CH_3)_3$, neutralization of **III** may proceed through several pathways, including transfer of the methyl cation to the walls of the reaction vessel or to adventitious acceptors, initially present in the mixture or generated by its radiolysis.

[11] S. G. Lias, E. P. L. Hunter, *J. Phys. Chem. Ref. Data* **1998**, *27*, 413.

[12] Preparation of these standard compounds has been carried out according to: P. J. Stang, M. G. Mangum, *J. Am. Chem. Soc.* **1975**, *97*, 1459.

[13] Thermochemical data of the reaction in Scheme 3 as calculated at the B3LYP/6-31G* level of theory (onium ion, neutral olefin, $-\Delta H_{298}$ [kcal mol^{-1}]): **Ia**, **4E**, 28.5; **Ia**, **4Z**, 30.1; **Is**, **4E**, 32.0; **Is**, **4Z**, 33.6; **II**, **4E**, 29.1; **II**, **4Z**, 30.7. Eliminative ring opening may be accompanied by nucleophilic addition of $N(CH_3)_3$ to the onium ion with formation of the $[Me_3NCHMeCHMeOMe]^+$ intermediate and by nucleophilic transfer of the CH_3 group from the onium ion to $N(CH_3)_3$ to give back the starting epoxide and $N(CH_3)_4^+$ (see the Supporting Information). The hypothesis that olefins **4E** and **4Z** may be formed by elimination of $HN(CH_3)_3^+$ from the $[Me_3NCHMeCHMeOMe]^+$ intermediate is ruled out by the lack of any detectable products from the $[Me_3NCHMeCHMeOMe]^+$ intermediate, which is generated by gas-phase methylation of *threo*-$Me_2NCHMeCHMeOMe$ by $(CH_3)_2F^+$ under conditions identical to those of Table 1.

[14] $\Delta G_{298}(\mathbf{4E}) - \Delta G_{298}(\mathbf{4Z}) = +1.3$ kcal mol^{-1}. See also E. Dodziuk, H. von Voithenberg, N. L. Allinger, *Tetrahedron* **1982**, *38*, 2811, and references therein.

[15] The O-C_β-C_α-H$\cdots$$NH_3$ dihedral angles of **IVs** and **IVa** calculated at the B3LYP/6-31G* level of theory are 100.4 and 97.0°, respectively.

[16] Back-dissociation of the hydrogen-bonded adducts opens the way for the competing nucleophilic substitutions mentioned in reference [13], involving reattack of $N(CH_3)_3$ at the carbon centers of the freed onium ion. Thus, only a fraction of the back-dissociating hydrogen-bonded adducts collapse again to another hydrogen-bonded adduct.

[17] Interaction of $(CH_3)_3N$ with the ring hydrogen atoms of **II** generates an initial distribution of [**IVa**^{t}] ≈ [**IVs**^{t}] which is not far from that corresponding to the thermodynamic equilibrium ([**IVa**^{t}]$_{eq}$ ≈ [**IVs**^{t}]$_{eq}$). Thus, the slight positive temperature dependence of the **4E**:**4Z** ratios from **2** reflects the effect of temperature on the ring-opening processes and on the limited **IVs**^{t} ↔ **IVa**^{t} interconversion. In contrast, interaction of $(CH_3)_3N$ with the ring hydrogen atoms of the **Is**/**Ia** pair generates the corresponding adducts in an initial distribution of [**IVa**^{c}] and [**IVs**^{c}] which is far away from the equilibrium distribution ([**IVs**^{c}]$_{eq}$ > [**IVa**^{c}]$_{eq}$). In this case, the steeper positive temperature dependence of the **4E**:**4Z** ratios from **1** is much more sensitive to the effect of temperature on the **IVa**^{c} → **IVs**^{c} conversion, which efficiently competes with the ring-opening reactions.

[18] M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Repogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzales, J. A. Pople, *Gaussian 94*, *Revision E. 2*, Gaussian, Inc., Pittsburg, PA, **1995**.

[19] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[20] C. Gonzales, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.

High Oxidation State Organocobalt Complexes: Synthesis and Characterization of Dihydridodisilyl Cobalt(V) Species[**]

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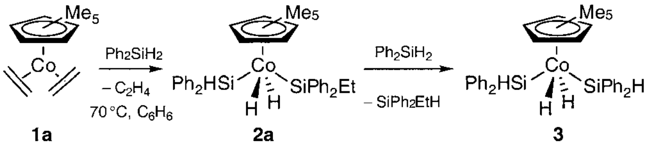
Peter S. White

Recently there has been considerable interest in the organometallic chemistry of late transition metals in high oxidation states. Second- and third-row metals in particular were stabilized in high oxidation states by using organic ligand environments. Certain catalytic reactions mediated by these late metals were proposed to occur through high oxidation state intermediates, as opposed to the traditionally formulated redox pairs.[1–4] Some of the most thoroughly investigated examples in this class are the high oxidation state neutral iridium(V) and rhodium(V) complexes studied initially by Maitlis et al. such as $[(C_5Me_5)IrMe_4]$,[5] $[(C_5Me_5)Ir(H)_2(SiR_3)_2]$, and $[(C_5Me_5)Rh(H)_2(SiR_3)_2]$[6–10] and the Ir^V complex cation $[(C_5Me_5)IrMe_3L]^+$ reported later by Bergman and Aliamo.[11] Higher oxidation states of first-row metals have been discussed as reactive intermediates, but isolated examples are rare.[12] We showed that cationic cobalt(III) alkyl complexes $[(C_5Me_5)\{P(OMe)_3\}CoR]^+$ are olefin hydrosilylation catalysts and must proceed through the Co^V intermediate $[(C_5Me_5)\{P(OMe)_3\}Co(R)(H)(SiR_3)]^+$ or the Co^{III} intermediate $[(C_5Me_5)\{P(OMe)_3\}Co(R)(\eta^2\text{-H–SiR}_3)]^+$.[13, 14] Here we report the synthesis and X-ray crystallographic characterization of a bis-hydrido bis-silyl cobalt(V) complex.

For cobalt-mediated bond-activation reactions we have used olefin complexes of the type $[(C_5Me_5)Co(olefin)_2]$ (**1**) as catalysts,[13, 15–17] which provides a source of $[(C_5Me_5)Co]$ through olefin dissociation.[18] Heating a solution of **1a** in C_6D_6 (olefin = C_2H_4) with 5 equiv of Ph_2SiH_2 (15 min, 70 °C) led to a rapid disappearance of starting material and, along with the appearance of ethylene and $Ph_2(Et)SiH$, the formation of two products **2a** and **3** in approximately 1:1 molar ratio, as determined by ^1H NMR spectroscopy [Eq. (1)].[19] Equivalent hydrido ligands and silyl methylene protons support a *trans* configuration of **2a**, while a single set of ^{13}C phenyl signals indicates a *trans* configuration for **3**.



(1)

Heating **1a** with an excess of Ph_2SiH_2 (5–10 equiv) in toluene at 85 °C for 60 min and removal of volatiles resulted in quantitative formation of **3**. Extraction with pentane and crystallization at −25 °C produces white crystals that are stable to air in the solid state and can be stored indefinitely at 20 °C in an argon atmosphere. In the temperature range of −80 to 70 °C no reactivity or dynamic behavior of **3** was observed by NMR spectroscopy. No exchange or magnetization transfer between the Co–H and the Si–H groups was observed on the NMR timescale, and silicon satellites for the Co–H signals were absent. On the basis of this spectroscopic evidence, the new cobalt silyl hydrido complexes are formulated as rare examples of organocobalt(V) species which contribute to a now complete series of silyl hydride complexes of the type $[(C_5Me_5)M(SiR_3)_2(H)_2]$ (M = Co, Rh, Ir).[6–10]

The activation of the Si–H bond is facile in this process, as is suggested by the reactivity of the more labile cobalt(I) precursor $[(C_5Me_5)Co(C_2H_3SiMe_3)_2]$ (**1b**). The reaction of **1b** with Ph_2SiH_2 (15 equiv) in C_6D_6 at 30 °C for 10 h gave a reaction mixture consisting of $[(C_5Me_5)Co(SiPh_2C_2H_4SiMe_3)(SiPh_2H)(H)_2]$ (**2b**) (70 %) and a minor amount of **3**. Heating this reaction mixture at 80 °C for 2 h resulted in quantitative formation of **3**. The reaction of Ph_2SiH_2 with

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