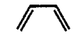
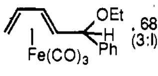
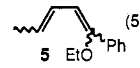
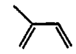
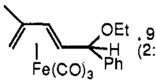
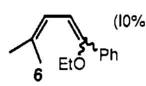
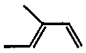
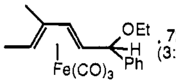
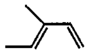
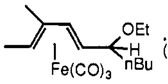
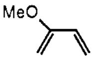
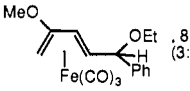
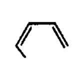
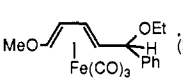
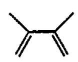
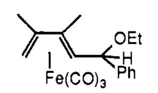
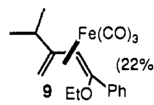
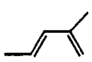
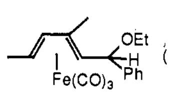
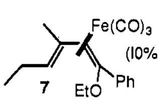
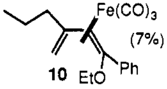
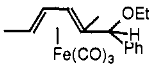
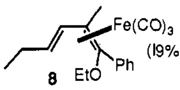
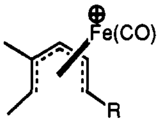
Table I. Coupling of 1,3-Dienes with Complexes **1a** and **1b**

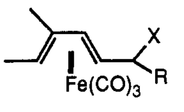
entry	complex	1,3-diene	products yield (diastereomer ratio)	byproducts (yield)
1.	Ia		 , 68%[a] (3:1)	 **5** (5%)[b]
2.	Ia		 , 90% (2:1)	 **6** (10%)[c]
3.	Ia		 , 72% (3:1)	---
4.	Ib		 , 68% (4:1)	---
5.	Ia		 , 87% (3:1)	---
6.	Ia		 , 83% (2:1)	---
7.	Ia		 , 42% (--)[d]	 **9** (22%)
8.	Ia		 , 23% (2:1)[e]	 **7** (10%)  **10** (7%)
9.	Ia		 , 0%	 **8** (19%)

[a] This yield includes a 20% yield of the uncomplexed diene. [b] A mixture of geometrical isomers was obtained. [c] A single isomer was obtained but the configuration has not been established. [d] Only one isomer was isolated. [e] The major isomer could not be obtained pure; the structure assignment is tentative.

which are powerful electrophiles.[6] The 5-ethoxy substituent is particularly convenient for conversion to the activated η^5-pentadienyl system. When the major adduct from 4-methyl-1,3-pentadiene (entry 3) was allowed to react with perchloric acid (70%) in acetic anhydride at 0 °C, the salt **11** was produced as orange crystals in 99% yield.[7] Reaction of **11** with D_2O in an NMR tube



11: R=Ph
14: R=nBu



12: X=OD, R=Ph
13: X=CH(CO$_2$Et)$_2$, R=Ph
15: X=CH(CO$_2$Et)$_2$, R=nBu

produced the alcohol **12** in high yield, as a single diastereomer.[8] Addition of diethyl sodiomalonate at 25 °C converted **11** into adduct **13**, in 81% yield, again as a single diastereomer. Similarly, the major diene complex in the table, entry 4 (from the n-butylcarbene complex **1b** and 4-methyl-1,3-pentadiene) was converted to the salt **14** (brown oil, 83%). Reaction of **14** with diethyl sodiomalonate gave a mixture of products from which isomer **15** could be obtained in 25% yield.

A mechanism for the (carbene)iron/diene coupling is postulated in Figure 1 by using as an example 2-methyl-1,3-pentadiene because the substrate leads to all three product types: the major product of type **4**, the diene positional isomer **7**, and the further rearrangement product **10** (Table I, entry 8). The first step is likely to be dissociation of CO and η^2-coordination of the less substituted double bond of the 1,3-diene, although we have not probed for direct evidence on this point. The failure of more highly alkyl substituted dienes is consistent with poor coordination of such species to low-valent iron. Formation of a vinyl-substituted ferracyclobutane (**16**) is proposed, which can undergo β-H elimination to give Fe(II) hydride complexes **17a** and **17b** or their η^3-allyl equivalent. Reductive-elimination from **17a** gives the product of type **4**, usually the major product, while the same process from **17b** produces the simple diene positional isomer **7**.[9] Alternatively, the iron–hydride unit can add across C-4/C-5 in **17b** to produce a new ferracyclobutane, **18**. Now β-H elimination followed by reductive elimination gives **10**. We imagine that a substituent at C-3 in **17a** disfavors reductive elimination to the product type **4** due to the formation of a highly substituted 1,3-diene ligand, while formation of **7** or **10** is favored by an electronic effect of the phenyl and/or ethoxy groups. Further characterization of the pathway and full elaboration of the coupling process is under way.

Acknowledgment is made to the National Science Foundation and the National Institutes of Health for generous support of our programs. We thank Dr. D. Little for collecting the mass spectral data.

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[6] Formation of (η^5-cyclohexadienyl)Fe(CO)$_3$ cations by hydride abstraction from (η^4-1,3-cyclohexadiene)Fe(CO)$_3$ complexes is a general technique which has been developed as the first stage of the synthesis methodology for coupling nucleophiles with cyclohexadienyl ligands. For a review, see: Birch, A. J. *J. Organomet. Chem.* **1985**, *285*, 267.

[7] The open (η^5-pentadienyl)Fe(CO)$_3$ cationic complexes have been much less developed compared to the η^5-cyclohexadienyl analogues, partly for lack of general methods of preparation. However, for examples and leading references, see: (a) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans.* **1976**, 954. (b) Bonner, T. G.; Holder, K. A.; Powell, P. *J. Organomet. Chem.* **1974**, *77*, C37. The protonolysis method of formation used here is adapted from: Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955.

[8] Nucleophile addition to η^5-pentadienyl ligands is known to be highly stereoselective for the ψ-exo isomer. For examples, see ref 4. See also: Maglio, G.; Musco, A.; Palumbo, R. *J. Organomet. Chem.* **1971**, *32*, 127.

[9] The overall cycloaddition of olefins with carbene ligands followed by β-hydrogen elimination and reductive elimination is rare; for a discussion and leading references, consult ref 2a. However, each step is well precedented.

Dehydrogenation and Cracking of n-Butane with Gas-Phase Ni$_n^+$, Pd$_n^+$, and Pt$_n^+$ Cluster Ions

Thomas F. Magnera, Donald E. David, and Josef Michl*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received October 17, 1986

The reactivity of small transition-metal particles as a function of their size has been of considerable interest in bridging the gap between homogeneous and heterogeneous catalysis.[1] An obvious approach is to investigate the reactivity of transition-metal clusters or cluster ions[2] as a function of size. Although some reports of such work with neutral clusters have appeared,[3] progress with cluster ions has been hampered by the poor availability of intense sources. Sputtering by kiloelectronvolt atoms or ions promises to be such a source.[4] We now report an extension of our previous

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* Present address: Department of Chemistry, University of Texas at Austin, Austin, TX 78712-1167.

[1] Somorjai, G. A. *Chemistry in Two Dimensions: Surfaces*; Cornell University Press: Ithaca, NY, 1981.

[2] Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.

[3] For instance, Geusic, M. E.; Morse, M. D.; Smalley, R. E. *J. Chem. Phys.* **1985**, *82*, 590.

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Table I. Relative Product Abundances for Reactions of Cluster Ions with *n*-Butane[a]

$$M_n^+ + C_4H_{10} \rightarrow X + Y^+$$

M_n^+	X: H_2 Y: $M_n^+C_4H_8$	$2H_2$ $M_n^+C_4H_6$	$3H_2$ $M_n^+C_4H_4$	CH_4 $M_n^+C_3H_6$	C_2H_6 $M_n^+C_2H_4$	C_2H_8 $M_n^+C_2H_2$	$M + C_2H_6$ $M_{n-1}^+C_2H_4$
Ni^+	6.0			1.1	9.8		
Ni_2^+	0.8	4.1	0.03		0.7	0.6	2.3
Ni_3^+	0.8	1.7	0.5				
Ni_4^+		1.3					
Ni_5^+		1.6					
Ni_6^+		0.2	0.7				
Ni_7^+			0.3				
Ni_8^+			0.6				
Ni_9^+			0.3				
Ni_{10}^+			0.5				
Pd^+	0.2			0.49	1.6		
Pd_2^+		16.0					
Pd_3^+		14.0					
Pd_4^+		0.3	0.3				
Pt^+		11		<0.5	1		
Pt_2^+			18			2.0	3.2

[a] M_n^+ intensity: 100.0.

Table II. Reactions of Ni_n^+ with *n*-Butane: Internal Ion Energy Effects[a]

M_n^+		$M_n^+C_4H_8$	$M_n^+C_4H_6$	$M_n^+C_4H_4$	$M_{n-1}^+C_2H_4$	M_{n-1}^+
Ni_2^+	collision cooled	6.7	8.1		1.7	0.3
	directly sputtered	0.8	4.1	0.02	2.3	3.8
Ni_3^+	collision cooled		3.0			
	directly sputtered	0.8	1.4	0.5		2.0

[a] M_n^+ intensity: 100.0.

investigations of the properties of cluster ions produced by the bombardment of frozen gases[5-9] to an investigation of the reactions of the gas-phase Ni_1^+–Ni_{10}^+, Pd_1^+–Pd_4^+, and Pt_1^+,Pt_2^+ ions with *n*-butane, using the previously described[7-10] triple-quadrupole secondary-ion mass spectrometer.

A metal target was bombarded by fast (~8 keV) Ar atoms. The ejected ions were velocity-selected in an electrostatic filter (Bessel box), mass-selected in the first quadrupole, and guided through the second quadrupole (rf only) filled with *n*-butane (10^{-4}–10^{-5} torr). The ions underwent single collisions at energies of ~1 eV or less, imposed by the spread in ion kinetic energies. The daughter ions resulting from reactions were analyzed in the third quadrupole.

Typical spectra are shown in Figure 1 and the results are summarized in Table I. The results for Ni^+ agree with those reported earlier, which have been attributed[11] to the initial insertion of the transition-metal ion into a C–C or C–H bond, ultimately resulting in dehydrogenation, (1), or cracking, (2,3).

$$Ni^+ + C_4H_{10} \rightarrow Ni^+(C_4H_8) + H_2 \tag{1}$$

$$Ni^+ + C_4H_{10} \rightarrow Ni^+(C_3H_6) + CH_4 \tag{2}$$

$$Ni^+ + C_4H_{10} \rightarrow Ni^+(C_2H_4) + C_2H_6 \tag{3}$$

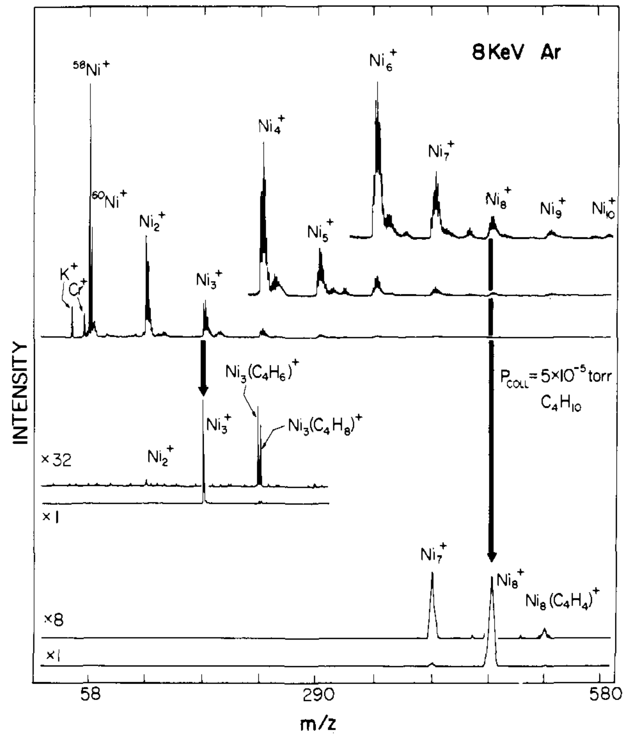

Figure 1.

The Pd^+ ion behaves similarly.[12] With Pt^+, the dehydrogenation process proceeds further, with an overall loss of $2H_2$.

Two obvious trends appear as the number of metal atoms *n* increases in the two cluster series available, Ni_n^+ and Pd_n^+: (i) the cracking reaction is suppressed; (ii) the extent of dehydrogenation increases.

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(4) (a) Fayet, P.; Wöste, L. *Surf. Sci.* **1985**, *156*, 134. (b) Hanley, L.; Anderson, S. L. *Chem. Phys. Lett.* **1985**, *122*, 410. (c) Freas, R. B.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 6202. (d) Freas, R. B.; Campana, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 4659. (e) Hanley, L.; Anderson, S. L. *Chem. Phys. Lett.* **1986**, *129*, 429.

(5) Michl, J. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *53*, 255.

(6) David, D. E.; Magnera, T. F.; Tian, R.; Michl, J. *Radiat. Eff.* **1986**, *99*, 247.

(7) David, D. E.; Magnera, T. F.; Tian, R.; Stulik, D.; Michl, J. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1986**, *14*, 378.

(8) Magnera, T. F.; David, D. E.; Tian, R.; Stulik, D.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 5040.

(9) Magnera, T. F.; David, D. E.; Michl, J. *Chem. Phys. Lett.* **1986**, *123*, 327.

(10) Magnera, T. F.; David, D. E.; Stulik, D.; Orth, R. G.; Jonkman, H. T.; Michl, J., unpublished results.

(11) (a) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129. (b) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293. (c) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736. (d) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; Bowers, M. T., preprint, 1986.

(12) The same products from the Pd^+ reaction have been very recently independently observed by others: Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5675. The relative abundances of the products are different, possibly due to electronic excitation in sputtered Pd^+.

The dehydrogenation activity of Pd_n^+ exceeds that of Ni_n^+; e.g., Ni_4^+ removes only $2H_2$ whereas Pd_4^+ removes $3H_2$. It appears that Pt_n^+ is even more active, and already Pt_2^+ removes $3H_2$.

In order to ascertain whether the reactivity differences are intrinsic or due to different electronic or vibrational internal energies ("temperature")[4b,13] of the clusters, we have attempted to cool them by collisions with an inert room-temperature gas. The clusters were sputtered into a 1-cm-long pressure cell filled with argon ($>10^{-1}$ torr) and extracted with a weak electric field (2-5 V/cm) through a 1-mm orifice. It is estimated that the ions undergo between 10 and 100 collisions with argon atoms. In the absence of argon, virtually no ions are detected, confirming that collisions are indeed occurring and are necessary for the ions to reach the vicinity of the cell exit.

The results obtained with collision-cooled cluster ions are compared to those from the simple sputtering experiments in Table II. Directly sputtered ions are much more likely to undergo dissociative collisions leading to Ni_{n-1}^+ and thus clearly have higher internal energies. They are also more likely to cause C–C bond breaking in butane while the ions cooled by argon gas collisions are more likely to dehydrogenate it. The probability of an exoergic bimolecular reaction in the absence of an activation barrier increases as the total energy available to the reacting pair decreases.[14] The opposite is true for endoergic reaction coordinates. We find that dehydrogenation by the Ni_n^+ clusters follows the behavior expected of exoergic reactions with no activation barrier. Cracking, on the other hand, appears to be endoergic, becoming more probable as the energy of the system increases.

We conclude that the trends in dehydrogenation activity displayed in Table I reflect the intrinsic reactivities of the cluster ions, while the variation in their tendency to break C–C bonds may be at least in part due to differences in their internal energy.

Acknowledgment. This work was supported by Grant CHE 84-21118 from the National Science Foundation. We are grateful to Prof. J. L. Beauchamp for sharing his unpublished results with us.

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(13) Elkind, J. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1986**, *108*, 2765.

(14) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784.

New Lumibleomycin-Containing Thiazolylisothiazole Ring

Takashi Morii, Isao Saito, and Teruo Matsuura

Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Sakyo-ku, Kyoto 606, Japan

June Kuwahara and Yukio Sugiura*

Faculty of Pharmaceutical Sciences, Kyoto University
Sakyo-ku, Kyoto 606, Japan

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In contrast to the recognition of AT-rich sites in the minor groove of B DNA by small molecules such as netropsin and distamycin,[1] GC recognition elements have not been well understood. Antitumor antibiotic bleomycin preferentially attacks guanine-pyrimidine (5′ → 3′) sequences, in particular GC sites.[2] The bithiazole moiety of bleomycin has been supposed to play a key role in its sequence-specific interaction with DNA.[3] However, there is much current controversy on the nature of the binding mode of the bithiazole group to DNA.[3-7] In this respect, a specific modification of the bithiazole group without alteration of the other part is extremely useful. Our previous work demonstrated that changing of the 2,4′-bithiazole group to 4,4′-bithiazole did not alter the sequence specificity in DNA cleavage.[8] We now wish to report a novel bleomycin, lumibleomycin, bearing a new ring system of thiazolylisothiazole as the DNA binding site. The chemical structures of bleomycin antibiotics used in this study are given in Figure 1.

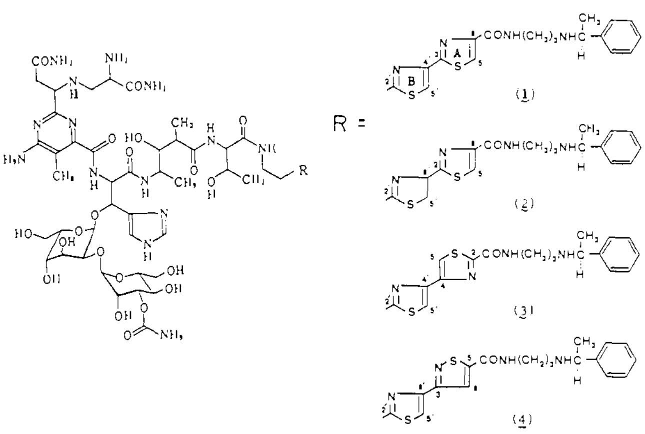

Figure 1. Chemical structures of original peplomycin (PEM, 1), phleomycin (2), photoPEM (3), and lumiPEM (4).

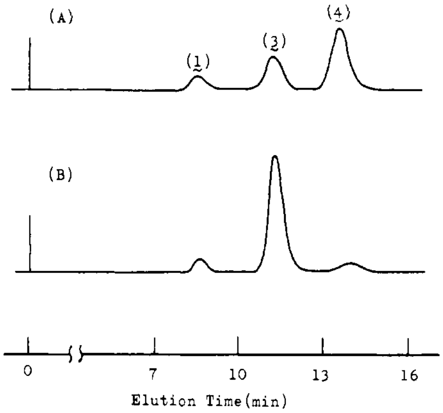

Figure 2. HPLC analyses of UV-irradiated 5:1 Cu(II)–PEM(A) and 1:1 Cu(II)–PEM(B) systems.

In our previous paper,[8] light irradiation of a 1:1 peplomycin (PEM, 1)–Cu(II) complex system resulted in an isomerization of the 2,4′-bithiazole ring to 4,4′-bithiazole to produce photoPEM (3) preferentially, together with a small amount of byproduct. As clearly shown in Figure 2, however, the present irradiation (302-nm light) of a 1:5 PEM–Cu(II) system dramatically enhanced the formation of this minor product (retention time, 13.4 min).[9] Thus the new phototransformed bleomycin, termed "lumiPEM", was isolated by preparative HPLC in 30% yield, and the structure was assigned as **4** on the basis of spectral data. Particularly useful for the structural assignment is the comparison of the spectral data with those of the model compound methyl

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(3) Riordan, J. M.; Sakai, T. T. *J. Med. Chem.* **1983**, *26*, 884–891.

(4) Chien, M.; Grollman, A. P.; Horwitz, S. B. *Biochemistry* **1977**, *16*, 3641–3647.

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(9) A solution containing PEM (5×10^{-5} M) and $CuSO_4$ (2.5×10^{-4} M) in 10 mM Tris-HCl buffer (pH 7.5, 5 mL) was irradiated with an ultraviolet 60-W transilluminator through a Pyrex tube for 15 min. After evaporation of the reaction solution, the residue was subjected to HPLC, using a Nova-PAK ${}_4C_{18}$ ODS column, and eluted with the solvent (1% aqueous CH_3COONH_4/CH_3CN, 85:15; flow rate, 2.5 mL/min).