than that in **1**$^{\bullet}$, **2**$^{\bullet}$ has the lower vertical ionization potential. However, relaxation from the geometry of the radical to the geometry of the cation, which stabilizes **1**$^{+}$ by 21.2 kcal/mol, stabilizes **2**$^{+}$ by only 13.2 kcal/mol. The optimized bond angles at the bridgehead carbon go from 111.0° and 2 × 103.9° in **1**$^{\bullet}$ to 120.2° and 2 × 111.6° in **1**$^{+}$. The more rigid cubyl skeleton permits much less planarization at the cationic carbon in **2**$^{+}$, so that, on going from **2**$^{\bullet}$ to **2**$^{+}$, the bond angles at this carbon increase from 91.8° to only 98.3°.[18] The greater relaxation energy of **1**$^{+}$ is responsible for the finding that, at the RHF level, it is predicted to be formed from the corresponding hydrocarbon 4.6 kcal/mol more readily than **2**$^{+}$.[19]

Delocalized species in general[20] and nonclassical carbocations in particular[21] are stabilized, relative to localized classical structures, by inclusion of electron correlation. Therefore, it is not surprising that, with inclusion of electron correlation at the MP2 level, **2**$^{+}$ is selectively stabilized, so that its formation from **2**-H is now calculated to require 7.3 kcal/mol *less* energy than formation of **1**$^{+}$ from **1**-H.[22] A 3-21G vibrational analysis confirmed that **2**$^{+}$ is a true MP2 energy minimum.

C–H hyperconjugation does not appear to be very important for stabilizing **2**$^{+}$. As with **2**$^{\bullet}$, the α C–H bond length is the shortest in **2**$^{+}$. A Mulliken population analysis of the 6-31G* RHF wave function for **2**$^{+}$ finds the charge (0.31) at each of the α hydrogens to be only marginally greater than that (0.29) at each of the β hydrogens and at the γ hydrogen. Given the apparent unimportance of C–H hyperconjugation, it is not surprising that a degenerate 1,2-hydrogen shift in **2**$^{+}$ is calculated to have a very substantial barrier of 54.3 kcal/mol at the 6-31G* RHF level and 41.2 kcal/mol with MP2.

The population analysis reveals, surprisingly, that the γ C–H group is about as positively charged (0.16) as each of the α C–H groups and more positively charged than each of the β C–H groups (0.05). The additional finding of a positive bond order between the electron-deficient p orbital at the cationic carbon and the p orbital, aligned with it, at each of the three β carbons suggests that some stabilization of **2**$^{+}$ comes from delocalization of the electrons in the α,β and β,γ C–C bonds. The fact that this delocalization results in *three* cross-ring bonding interactions to the cationic carbon in **2**$^{+}$ is presumably responsible, at least in part, for the result that each corresponding cross-ring distance (2.100 Å with 3-21G and 2.039 Å with 6-31G* RHF optimizations) is considerably longer than that calculated for cations, like bicyclobutonium[23] and bridgehead bicyclo[*n*.1.1]alkylium,[24] in which there is only one such interaction. The relative weakness of the individual, cross-ring, bonding interactions in **2**$^{+}$ is probably why each of the six, α,β C–C bonds lengthens by only about 0.02 Å on formation of **2**$^{+}$ from **2**-H and why the length of the three β,γ bonds remains almost unchanged.

On the basis of the results of the population analysis of **2**$^{+}$, the presence of σ electron withdrawing substituents at the α or γ carbons would be expected to destabilize the carbocation more than at the β carbons. However, because the γ C–H bond lies along the axis of the cylindrically symmetrical LUMO of **2**$^{+}$, π-donor substituents at the γ carbon should not be effective at stabilizing the carbocation. Computational tests of these qualitative predictions are in progress. Experimentally, Eaton and Moriarty have already found that electron-withdrawing substituents at the γ carbon greatly retard the rate of carbocation formation and that the presence of a methyl group—a π but not a σ donor—at this carbon atom also has a small, rate-retarding effect.[6]

Acknowledgment. We thank the National Science Foundation for support of this research and for providing funds for the purchase of the Convex C-2 computer, on which some of these calculations were performed. We also thank the San Diego Supercomputer Center for a generous allocation of time on the Cray XMP-48 computer at SDSC.

Registry No. 2-Methylpropane, 75-28-5; *tert*-butyl cation, 14804-25-2; *tert*-butyl radical, 1605-73-8; bicyclo[2.2.1]heptane, 279-23-2; bicyclo[2.2.1]heptyl cation, 21898-87-3; bicyclo[2.2.1]heptyl radical, 2697-23-6; cubane, 277-10-1; cubyl cation, 125665-92-1; cubyl radical, 67151-55-7.

Supplementary Material Available: Optimized geometries and energies for the hydrocarbons, radicals, and cations discussed in the paper (26 pages). Ordering information is given on any current masthead page.

---

[18] The pyramidal geometry at this carbon is presumably responsible for the finding that its chemical shift, δ 384.9, relative to methane, is calculated to be unusually large. We are indebted to Professor Paul Schleyer for performing IGLO chemical shift calculations on **2**$^{+}$ and communicating the results to us.

[19] The hydrocarbons appear to be satisfactory reference compounds, since at the 6-31G* RHF level formation of **2**$^{+}$ from **2**-OH is calculated to require 20.7 kcal/mol more energy than formation of $(CH_3)_3C^+$ from $(CH_3)_3COH$. This value agrees well with the 20.2 kcal/mol energy difference computed when the hydrocarbons are used as the reference compounds.

[20] For examples and a discussion, see: Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783 and references therein.

[21] For examples, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; pp 379–396. Raghavachari, K.; Haddon, R. C.; Schleyer; P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 5915. Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185. Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300.

[22] The MP2 relaxation energies of −22.2 kcal/mol for **1**$^{+}$, −13.9 kcal/mol for **2**$^{+}$, and −12.6 kcal/mol for $(CH_3)_3C^+$ are all very close to those computed at the RHF level. Thus, the selective stabilization of **2**$^{+}$ by inclusion of electron correlation cannot be attributed to an increase in the magnitude of its relaxation energy. In fact, formation of **2**$^{+}$ from **2**-H is calculated at the MP2 level to require 15.6 kcal/mol less energy than formation of **1**$^{+}$ from **1**-H when the energies of the cations are each computed at the geometry of the corresponding radical.

[23] McKee, M. L. *J. Phys. Chem.* **1986**, *90*, 4908. Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325. Saunders, M.; Laidig, K.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652.

[24] Della, E. W.; Gill, P. M. W.; Schiesser, C. H. *J. Org. Chem.* **1988**, *53*, 4354.

Solvolyses of Cubyl Triflates. The Cubyl Cation[†,1]

Robert M. Moriarty,* Sudersan M. Tuladhar,
Raju Penmasta, and Alok K. Awasthi

University of Illinois at Chicago
Department of Chemistry
Box 4348, Chicago, Illinois 60680

Received November 1, 1989

Nucleophilic substitution reactions upon cubyl iodide are fundamentally limited by the structural impossibility of an S_N2 backside attack and by the assumed instability of the cubyl cation in an S_N1 solvolysis. In effect, in recent synthetic work,[2] we and others have circumvented these two pathways by using an oxidative nucleophilic displacement along the lines of the work of Wiberg et al.,[3] Kropp et al.,[4] and Zefirov et al.[5] While the exact nature of hypervalent iodine in oxidative displacement is not totally clear,[2] this work afforded us the series of 4-substituted triflates **2a–f**,[6]

[†] Dedicated to Professor Paul von Rague Schleyer on the occasion of his 60th birthday.

[1] A preliminary report of this work was made: Moriarty, R. M.; Tuladhar, S. M.; Penmasta, R.; Awasthi, A. K. Presented at the 198th National Meeting, of the American Chemical Society, Miami Beach, FL, Sept 10–15, 1989; paper ORGN 18.

[2] Moriarty, R. M.; Khosrowshahi, J. S. *Synth. Commun.* **1989**, *19*, 1395. See also: Eaton, P. E.; Kunkle, G. T. *Tetrahedron Lett.* **1986**, *27*, 6053.

[3] Wiberg, K. B.; Pratt, W. E.; Matturo, M. G. *J. Org. Chem.* **1982**, *47*, 2720.

[4] Davidson, R. I.; Kropp, P. J. *J. Org. Chem.* **1982**, *47*, 1904.

[5] Zefirov, N. S.; Zdhankin, V. V.; Kozmin, A. S. *Tetrahedron Lett.* **1986**, 1845.

[6] Synthesis of cubyl triflates: In a typical experiment, a mixture of cubyl iodide (1 mmol), $(C_6H_5IO)_n$ (3 mmol), and $(CH_3)_3SiOTf$ (3 mmol) in dry CH_2Cl_2 (50 mL) was stirred at room temperature for 1 h to several days, depending on the C_4 group: $H < CH_3 < CO_2CH_3 < Br, I, Cl$. After the usual workup, the product was purified by flash chromotography (using pentane) or microdistillation under vacuum, to produce the pure compound in 50–60% yield.

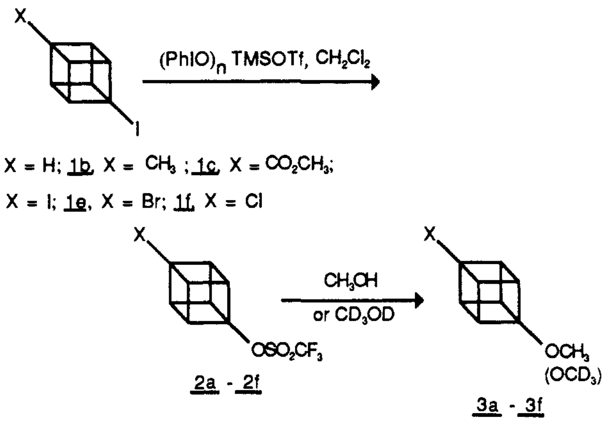
0002-7863/90/1512-3228\$02.50/0

Table I. First-Order Rate Constants for Methanolysis of 4-Substituted 1-Cubyl Triflates (**2a–e**)[a]

compd; X (4-X-cubyl)	temp, °C	rate constant: k, s^{-1}	$T_{1/2}$, min
2a; H	47	4.75×10^{-5}	243
	57.6	1.99×10^{-4}	58
	67.5	5.91×10^{-4}	19
	80	1.94×10^{-3}	6
	120	7.1×10^{-2}[b]	0.16
2b; CH_3	25	9.6×10^{-7}	12000
	120	2.2×10^{-2}[b]	0.52
2c; CH_3O_2C	120	6.6×10^{-4}	18
2d; I	120	3.8×10^{-6}	3040
2e; Br	120	1.3×10^{-6}	8885

[a] Determined by integration of NMR peaks at 400 MHz. [b] Calculated rate constant.

which are obviously appropriate substrates for the solvolytic reaction.

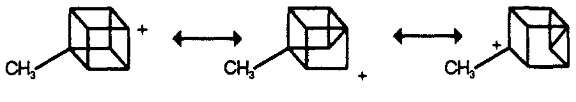


A priori, one would expect the pyramidalized cubyl cation to be of high energy. An early prediction based on quantitative conformational analysis had 1-cubyl triflate as completely inert, $k < 10^{-12}$ s^{-1} at 250 °C![7] The rate data reported in Table I indicate that the series of cubyl triflates **2a–e** solvolyze at measurable rates, to yield substitution products in which the cubyl system is retained, **2a–f** → **3a–f**.[6] The first question prompted by these observations is whether these are S_N1 reactions rather than bimolecular displacements. To clarify this issue, the nonnucleophilic polar solvent hexafluoroisopropyl alcohol was used, and the rate for **2c** at 75 °C was 1.25×10^{-5} s^{-1} and 4.15×10^{-6} at 62.4 °C,[8] compared with $k_{120} = 6.6 \times 10^{-4}$ s^{-1} for methanolysis. The Y value for adamantyl triflate in 97% HFIP is 2.51 while that in methanol is −0.79; assuming an m of 1, one would predict roughly a 10^3 rate difference, which is close to that observed.[9] This indicates an S_N1 process, as does the overall kinetic behavior in both solvent systems.

Accepting a carbocationic mechanism, the next questions involve, first, the rate of formation of the cubyl cation relative to other bridgehead systems and, secondly, the nature of the cubyl cation with respect to charge distribution, i.e., classical or nonclassical.

In an accompanying paper, Eaton et al. report on the unexpectedly rapid solvolysis of cubyl triflate, and in an additional accompanying communication, Hrovat and Borden report ab initio calculations on the cubyl cation.[10] Bridged or "nonclassical" versions of a cation are frequently associated with unusual stability. In the closely related homocubyl system, Rüchardt et al. invoke a nonclassical cation to explain an unexpectedly rapid rate of solvolysis.[11] We report results complementary to Eaton's that do not agree with a nonclassical structure for the cubyl cation. Inspection of the rate data in Table I reveals two striking features. First, the 4-methyl group is rate retarding by a factor of 3, and second, the polar C_4 substituents CO_2CH_3, Br, and I have very large rate-retarding effects relative to hydrogen.

One would expect the C_4 methyl group to stabilize positive charge at that position (**4a** ↔ **4c**) in a delocalized version of the cation.



4a 4b 4c

The use of a methyl probe for nonclassical extended delocalization has revealed this effect in rate accelerations in the case of 1-methylnorbornyl (58-fold,[12] 100-fold[13,14]), trishomocyclopropenyl (10-fold[15]), and cholesteryl (homoallylic, 20-fold,[16] 75-fold[17]). Absence of skeletal rearrangement is in agreement, but not exclusionary of a nonclassical ion in **2a–f** → **3a–f**.

Ingold has discussed the weakly electronegative effect of the methyl group,[18] and dipole moment measurements upon alkanes support this view.[19] Schleyer and Woodworth[20] find a 3-fold reduction in the rate of solvolysis of 4-methylbicyclo[2.2.2]octyl 2-brosylate, which parallels the 3-fold rate decrease we observed for **2b** for a similar spatially articulated methyl group.

The large rate retardation observed for the C_4 carbomethoxy, iodo, and bromo must be addressed. If positive charge were substantially located at C_4 in a delocalized cubyl cation, one would expect a correlation with Brown's σp^+ constants (CH_3, −0.311; CO_2CH_3, 0.482; Cl, 0.114; Br, 0.150; I, 0.135), which should result in an acceleration for CH_3, a small retardation for Cl, Br, and I, and a large retardation for CO_2CH_3.[21] In fact, the opposite is observed. The substituent effects follow, rather, an inductive order for **2a–e** characterized by Grob's constants $\sigma_1{}^q$: CH_3, 0.11; CO_2CH_3, 1.70; Cl, 2.51; Br, 2.65; I, 2.36.[22] Two mechanisms may be considered for the transmission of the electronic effect of the substituent. The first is a through-bond transmission.[23] Stock et al., in a study of the dissociation constants for 4-substituted cubane-1-carboxylic acids, provided convincing evidence that through-bond was not the mechanism of transmission but rather the alternative field effect or through-space electrostatic effect predominated.[24] The effect of transannular polar groups upon solvolytic reactions has been interpreted on the basis of through-space dipolar destabilization of a cationic center.[25-27]

---

(7) Bingham, R. C.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 3189, ref 73.

(8) Determined by D. N. Kevill and M. J. D'Souza, Northern Illinois University, 1989.

(9) Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 4821.

(10) We thank Professors Eaton and Borden for sending preprints. Eaton, P. E.; Yang, C.-X.; Xiong, Y. *J. Am. Chem. Soc.*, first of three papers in this issue. Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, second of three papers in this issue.

(11) Mergelsburg, I.; Langhals, H.; Rüchardt, C. H. *Chem. Ber.* **1983**, *116*, 360. 4-Homocubyl bromide, $k_{120}{}^{HIFP} = 1.3 \times 10^{-7}$ s^{-1}.

(12) Wilt, J. W.; Wagner, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 6135.

(13) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 3901.

(14) Lenoir, D. *Chem. Ber.* **1975**, *108*, 2055.

(15) Norin, T. *Tetrahedron Lett.* **1964**, 37. Based on four isomeric thujyl tosylates.

(16) deSousa, R. M.; Moriarty, R. M. *J. Org. Chem.* **1965**, *30*, 1509.

(17) Sneen, R. *J. Am. Chem. Soc.* **1958**, *80*, 3982.

(18) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: Ithaca, NY, and London, 1969; p 122.

(19) Lide, D. R.; Mann, D. E. *J. Chem. Phys.* **1959**, *29*, 914; **1960**, *33*, 1514, 1519.

(20) Schleyer, P. v. R.; Woodworth, C. W. *J. Am. Chem. Soc.* **1968**, *90*, 6528. The bicyclo[2.2.2]octyl cation is borderline nonclassical: the rate acceleration due to bridging is approximately $10^{0.9}$. As with **4c**, no delocalized structure has the positive charge at C_4.

(21) For a discussion, see: Vogel, P. *Carbocation Chemistry*; Elsevier: New York, 1985; pp 240–245.

(22) Grob, C. A.; Schaub, B.; Schlageter, M. G. *Helv. Chim. Acta.* **1980**, *63*, 57.

(23) Liotta, C. L.; Fisher, W. F.; Slighton, E. L.; Harris, C. L. *J. Am. Chem. Soc.* **1972**, *94*, 2129. Stock, L. M. *J. Chem. Educ.* **1972**, *49*, 400.

(24) Cole, T. W., Jr.; Mayers, C. J.; Stock, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4555.

(25) Moriarty, R. M.; Romain, C.; Lovett, T. O. *J. Am. Chem. Soc.* **1967**, *89*, 3927.

(26) Lenoir, D.; Röll, W.; Weiss, E.; Wenke, G. *Tetrahedron Lett.* **1976**, *23*, 1991.

(27) Oxer, G. W.; Wege, D. *Tetrahedron Lett.* **1971**, 457.

In the case of 4-carbomethoxybicyclo[2.2.2]octyl brosylate, $k_R/k_H = 7 \times 10^{-3}$ in acetolysis at 75 °C was observed.[20] A similar rate retardation by CO_2CH_3 was observed in the ethanolysis of 3-carbomethoxy-1-bromoadamantane.[20] We attribute the large rate retardation for **2a–e** to a highly effective transannular transmission of the polar effect of the positive end of the C–X dipole upon the incipient carbocationic center. Due to the absence of solvent in the interannular space, the effective dielectric constant of the interior cubyl cavity differs significantly from that of the bulk exterior solvent, and this accounts for the efficient transmission of the polar effect.[28]

The unusually rapid rate of solvolysis of cubyl triflate is not completely explained, but a considerable amount of quantitative theory has been devoted to rate acceleration due to through-space stabilization of cyclobutylium ion in bicyclo[*n*.1.1]alkylium cations.[29,30] A bicentric 1,3-interaction in the nondelocalized cubyl cation ought to be considered as a stabilizing feature.

Finally, in experiments with George Olah, we have had no success in observing the cubyl cation in the low-temperature NMR.

Acknowledgment. We thank the Office of Naval Research for support of this work under Contract FED ONR 83-K-0306. In addition, ongoing collaboration with Prof. Dennis N. Kevill of Northern Illinois University, Department of Chemistry, and valuable discussions with Prof. George A. Olah of the Donald P. and Katherine B. Loker Hydrocarbon Research Lab and Department of Chemistry at the University of Southern California are gratefully acknowledged.

Registry No. 1a, 74725-77-2; **1b**, 125762-85-8; **1c**, 122200-58-2; **1d**, 97229-08-8; **1e**, 111873-47-3; **1f**, 124225-25-8; **2a**, 125762-86-9; **2b**, 125762-87-0; **2c**, 122200-63-9; **2d**, 125762-88-1; **2e**, 125762-89-2; **2f**, 125762-90-5.

---

(28) The effective dielectric constant of space between polar groups has been discussed; see: Tanford, C. *J. Am. Chem. Soc.* **1957**, *79*, 5348. Westheimer, F. H.; Kirkwood, J. G. *J. Chem. Phys.* **1938**, *6*, 513.

(29) Mc Kee, M. L. *J. Phys. Chem.* **1986**, *90*, 4908.

(30) Della, E. W.; Gill, P. M. W.; Schiesser, C. H. *J. Org. Chem.* **1988**, *53*, 4354.

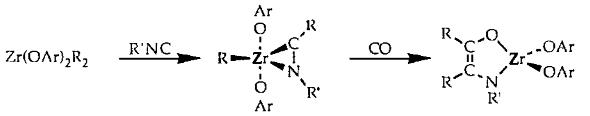
Reductive Coupling of Carbon Monoxide with Methyl Isocyanide in a Seven-Coordinate Niobium Complex

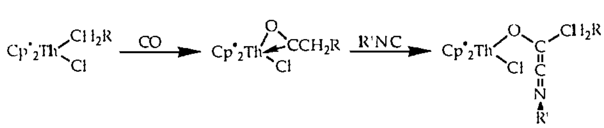
Edmund M. Carnahan and Stephen J. Lippard*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received December 14, 1989

Recently we elucidated several mechanistic steps in the reductive coupling of CO ligands in seven-coordinate tantalum and niobium dicarbonyl complexes.[1] Two-electron reduction of $[M(CO)_2(dmpe)_2Cl]$ first occurs with loss of halide to form a six-coordinate M(–I) species. Addition of 1 equiv of a trialkylsilyl halide next yields the (trialkylsiloxy)carbyne intermediate, $[M(\equiv COSiR_3)(CO)(dmpe)_2]$. Finally, addition of a second equivalent of R_3SiX induces CO–carbyne coupling to afford a bound bis(trialkylsiloxy)acetylene. Reductive coupling of isocyanide ligands in $[M(CNR)_6X]^+$ (M = Mo, W) complexes appears to occur by a completely analogous mechanism.[2] As details of these CO and CNR reductive coupling reactions became clarified, we were led to explore whether the reaction scheme would apply to cross-coupling between such linear, triply bonded ligands. The potential for coupling of carbon monoxide with an isocyanide was particularly intriguing, for the newly formed acetylene would contain the basic skeleton of amino acids. The coupling of an alkyl isocyanide and carbon monoxide is known to afford metal-bound enamidolate (eq 1)[3] or ketenimine (eq 2)[4] complexes. Both of these reactions involve acyl–isocyanide coupling. In contrast, coupling of C$\equiv$O and C$\equiv$NR according to the above mechanism should result in a bound $R_3Si(R)NC{\equiv}COSiR_3$ moiety. Here we report the synthesis of a new mixed isocyanide–carbonyl compound, $[Nb(CNMe)(CO)(dmpe)_2Cl]$ (**1**). When **1** is subjected to reductive coupling conditions, the complex $[Nb\{(Me_3Si)(Me)NC{\equiv}CO(SiMe_3)\}(dmpe)_2Cl]$, containing the unprecedented [(trimethylsilyl)methylamino](trimethylsiloxy)acetylene ligand, is formed.


(1)


(2)

Photolysis[5] for 10 min of a THF solution containing 0.1 g of $[Nb(CO)_2(dmpe)_2Cl]$[6] and 0.1 mL of CH_3NC resulted in a color change from orange to deep red. Upon workup, $[Nb(CNCH_3)(CO)(dmpe)_2Cl]$ was obtained as a red solid in 30–40% yield. Analytical data[7] supported the proposed formula, a complex in which a single CO has been replaced with methyl isocyanide. The infrared spectrum of **1** showed CO and CNR stretches at 1830 and 1752 cm^{-1}, indicative of an electron-rich metal center.[1a,8] Single-crystal X-ray structure determinations have been carried out on several such $[M(CNR)(CO)(dmpe)_2Cl]$ complexes.[9] All have short non-bonded C···C distances of ~2.4 Å for the C$\equiv$O and C$\equiv$NR ligands, small C–Nb–C angles of ~70°, and strongly bent (129–139°) C–N–R angles. These spectroscopic and structural data for the mixed isocyanide–carbonyl complexes indicate, on the basis of known criteria,[1,10] that they are good candidates for CO/CNR reductive coupling.

Addition of 40% Na/Hg[11] to a THF solution of **1** resulted in a color change from red to deep violet. This extremely reactive species has not yet been fully characterized, although the shift of the CO and CNR infrared bands to 1650 and 1590 cm^{-1} suggests the formation of $[Nb(CNMe)(CO)(dmpe)_2]^-$ by analogy to $[Ta(CO)_2(dmpe)_2]^-$.[1a] Upon addition of 2 equiv of Me_3SiCl, the violet solution slowly turned green over the course of an hour. The product exhibited no infrared stretches from 2800 to 1560 cm^{-1}, and the ^1H NMR spectrum showed the appearance of two trimethylsilyl resonances at δ 0.19 and 0.46 ppm. Analytical data[12]

---

(1) (a) Bianconi, P. A.; Vrtis, R. N.; Rao, Ch. P.; Williams, I. D.; Engler, M. P.; Lippard, S. J. *Organometallics* **1987**, *6*, 1968. (b) Vrtis, R. N.; Rao, C. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2669.

(2) Carnahan, E. M.; Lippard, S. J., to be submitted for publication.

(3) (a) McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072. (b) Latesky, S. L.; McMullen, A. K.; Niccolai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 1896. (c) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.

(4) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 56.

(5) Photolysis was performed by using a 450-W mercury Hanovia lamp filtered through Pyrex.

(6) (a) Burt, R. J.; Leigh, G. J.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 793. (b) Datta, S.; Wreford, S. S. *Inorg. Chem.* **1977**, *16*, 1134. (c) Bianconi, P. A. Ph.D. Thesis, Massachusetts Institute of Technology, 1986.

(7) Anal. Calcd for $C_{15}H_{35}NOP_4ClNb$ (**1**): C, 36.20; H, 7.09; N, 2.81; P, 24.89. Found: C, 36.23; H, 7.18; N, 2.74; P, 24.90. FTIR (KBr): 2967, 2901, 2850, 1830 (s), 1752 (s), 1420, 1391, 1245, 1279, 1140, 1100, 940, 930, 888, 727, 700, 641 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, 298 K): δ 3.18 (s, $CNCH_3$), 1.39 (br, PCH_3), 1.02 ppm (br, PCH_2).

(8) Caravana, C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1860.

(9) M = Nb, R = Cy; M = Ta, R = Et, *t*-Bu. Carnahan, E. M.; Bott, S. G.; Lippard, S. J., to be submitted for publication.

(10) Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263.

(11) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 1033.