

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.<sup>20</sup> A similar rate retardation by CO<sub>2</sub>CH<sub>3</sub> was observed in the ethanolysis of 3-carbomethoxy-1-bromoadamantane.<sup>20</sup> 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.<sup>28</sup>

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 cyclobutylum ion in bicyclo[*n*.1.1]alkylum cations.<sup>29,30</sup> 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.

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**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.

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

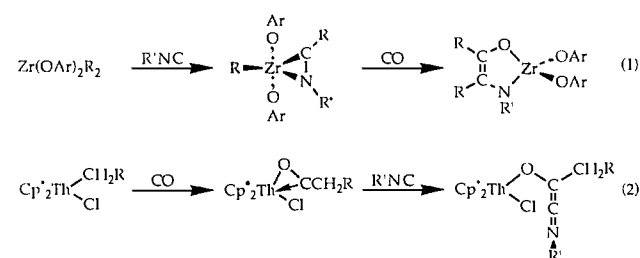
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Recently we elucidated several mechanistic steps in the reductive coupling of CO ligands in seven-coordinate tantalum and niobium dicarbonyl complexes.<sup>1</sup> Two-electron reduction of [M(CO)<sub>2</sub>(dmpe)<sub>2</sub>Cl] first occurs with 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(≡C(OSiR<sub>3</sub>))(CO)(dmpe)<sub>2</sub>]. Finally, addition of a second equivalent of R<sub>3</sub>SiX induces CO-carbyne coupling to afford a bound bis-(trialkylsiloxy)acetylene. Reductive coupling of isocyanide ligands in [M(CNR)<sub>6</sub>X]<sup>+</sup> (M = Mo, W) complexes appears to occur by a completely analogous mechanism.<sup>2</sup> 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 partic-

ularly 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)<sup>3</sup> or ketenimine (eq 2)<sup>4</sup> complexes. Both of



these reactions involve acyl-isocyanide coupling. In contrast, coupling of C≡O and C≡NR according to the above mechanism should result in a bound R<sub>3</sub>Si(R)NC≡COSiR<sub>3</sub> moiety. Here we report the synthesis of a new mixed isocyanide-carbonyl compound, [Nb(CNMe)(CO)(dmpe)<sub>2</sub>Cl] (**1**). When **1** is subjected to reductive coupling conditions, the complex [Nb(Me<sub>3</sub>Si)(Me)NC≡CO(SiMe<sub>3</sub>)](dmpe)<sub>2</sub>Cl, containing the unprecedented [(trimethylsilyl)methylamino][(trimethylsiloxy)acetylene] ligand, is formed.

Photolysis<sup>5</sup> for 10 min of a THF solution containing 0.1 g of [Nb(CO)<sub>2</sub>(dmpe)<sub>2</sub>Cl]<sup>6</sup> and 0.1 mL of CH<sub>3</sub>NC resulted in a color change from orange to deep red. Upon workup, [Nb(CNCH<sub>3</sub>)(CO)(dmpe)<sub>2</sub>Cl] was obtained as a red solid in 30-40% yield. Analytical data<sup>7</sup> 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<sup>-1</sup>, indicative of an electron-rich metal center.<sup>1a,8</sup> Single-crystal X-ray structure determinations have been carried out on several such [M(CNR)(CO)(dmpe)<sub>2</sub>Cl] complexes.<sup>9</sup> All have short non-bonded C...C distances of ~2.4 Å for the C≡O and C≡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,<sup>1,10</sup> that they are good candidates for CO/CNR reductive coupling.

Addition of 40% Na/Hg<sup>11</sup> 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<sup>-1</sup> suggests the formation of [Nb(CNMe)(CO)(dmpe)<sub>2</sub>]<sup>-</sup> by analogy to [Ta(CO)<sub>2</sub>(dmpe)<sub>2</sub>]<sup>-</sup>.<sup>1a</sup> Upon addition of 2 equiv of Me<sub>3</sub>SiCl, the violet solution slowly turned green over the course of an hour. The product exhibited no infrared stretches from 2800 to 1560 cm<sup>-1</sup>, and the <sup>1</sup>H NMR spectrum showed the appearance of two trimethylsilyl resonances at δ 0.19 and 0.46 ppm. Analytical data<sup>12</sup>

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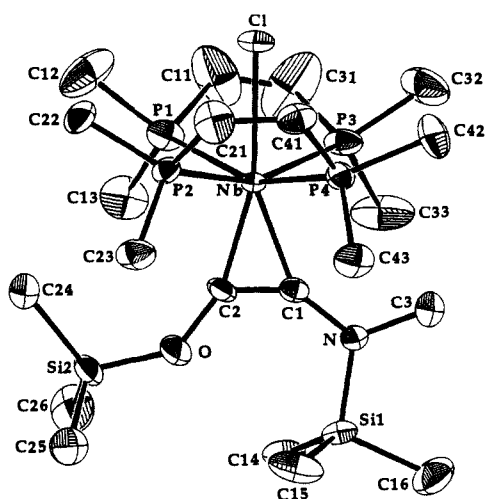
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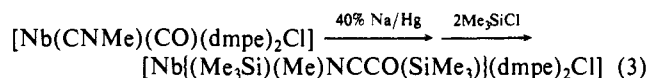
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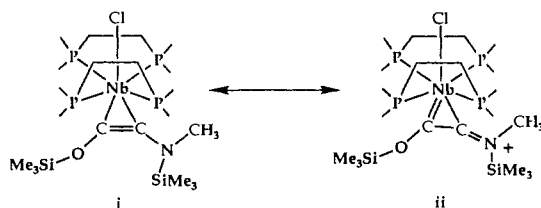


**Figure 1.** ORTEP diagram of **2** showing the 40% probability thermal ellipsoids. Hydrogen atom positions were calculated. Selected bond distances (Å) and angles (deg) are as follows: Nb–Cl, 2.125 (7); Nb–C2, 2.079 (7); Cl–C2, 1.30 (1); C1–N, 1.386 (9); C2–O, 1.385 (8); N–C3, 1.47 (1); N–Si1, 1.744 (6); O–Si2, 1.615 (6); Nb–P1, 2.573 (2); Nb–P2, 2.554 (2); Nb–P3, 2.562 (2); Nb–P4, 2.545 (2); Nb–Cl, 2.586 (1); C1–Nb–C2, 35.9 (3); Nb–C2–O, 158.7 (5); Nb–Cl–N, 149.5 (5); C2–O–Si2, 140.3 (6); Cl–N–Si1, 120.9 (5); Cl–N–C3, 118.8 (6); P1–Nb–P3, 76.93 (8); P1–Nb–P2, 98.74 (7).

were consistent with the formula  $[\text{Nb}(\text{Me}_3\text{Si})(\text{Me})\text{NCCO}(\text{SiMe}_3)](\text{dmpe})_2\text{Cl}$  (**2**), in which  $\text{C}\equiv\text{O}$  and  $\text{C}\equiv\text{NR}$  are reductively coupled to form a highly functionalized acetylene (eq 3).



The structure of **2** (Figure 1) was revealed by X-ray analysis of a green single crystal grown from pentane at  $-20^\circ\text{C}$ .<sup>13</sup> The geometry is distorted octahedral with the midpoint of the acetylene defining one vertex. The dmpe ligands are in an asymmetric envelope conformation<sup>14</sup> with the methylene linker chains pointing toward the chlorine atom. The coordinated  $\text{RR}'\text{NC}\equiv\text{COR}$  moiety is planar, indicating a delocalized electronic structure.<sup>15</sup> The acetylene is bound asymmetrically, however, with the Nb–Cl bond distance being 0.05 Å greater than that of Nb–C2. The difference indicates that resonance form ii plays a significant role in metal–ligand bonding. Functionalized acetylenes of the form



$\text{RR}'\text{NC}\equiv\text{COR}$  have not been isolated.<sup>16</sup> Although there are

(12) Anal. Calcd for  $\text{C}_{21}\text{H}_{33}\text{NOSi}_2\text{P}_4\text{ClNb}$  (**2**): C, 39.16; H, 8.29; N, 2.17. Found: C, 39.31; H, 7.67; N, 2.41. FTIR (KBr) 2960, 2897, 2802, 1550, 1420, 1396, 1243, 1147, 1086, 1003, 935, 889, 846, 752, 718, 680, 611, 447  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.65 (br,  $\text{PCH}_2$ ), 1.58 (br,  $\text{PCH}_3$ ), 1.22 (br,  $\text{PCH}_2$ ), 1.13 (br,  $\text{PCH}_3$ ), 0.46 ( $\text{SiMe}_3$ ), 0.19 ( $\text{SiMe}_3$ ) ppm.

(13) Crystal data ( $-70^\circ\text{C}$ ) for **2**:  $\text{C}_{21}\text{H}_{33}\text{NOSi}_2\text{P}_4\text{ClNb}$ ,  $M_r = 644.1$ , monoclinic, space group  $P2_1$  (No. 4),  $a = 10.204$  (5) Å,  $b = 18.475$  (1) Å,  $c = 9.776$  (5) Å,  $\beta = 115.51$  (2)°,  $Z = 2$ ,  $V = 1663$  (1) Å<sup>3</sup>,  $\rho_{\text{calcd}} = 1.29$   $\text{g cm}^{-3}$ . For 2870 unique reflections with  $F^2 > 3\sigma(F^2)$ ,  $R = 0.034$  and  $R_w = 0.042$ . Inversion of the coordinates and refinement of the other enantiomorph did not alter the  $R$  factors.

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several examples of the symmetric, metal-coordinated substituted acetylenes  $\text{ROC}\equiv\text{COR}$ <sup>1,17</sup> and  $\text{RR}'\text{NC}\equiv\text{CNRR}'$ ,<sup>10,15a,18</sup> to our knowledge **2** is the first example of the mixed  $\text{RR}'\text{NC}\equiv\text{COR}$  acetylene ligand.

In summary, reductive coupling of linear triply bonded ligands in seven-coordinate early transition metal complexes has been extended in a significant way to the cross-coupling of  $\text{C}\equiv\text{O}$  and  $\text{C}\equiv\text{NR}$ . This work demonstrates the generality of the reaction mechanism previously elucidated for both the isocyanide and carbon monoxide coupling schemes.

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**Supplementary Material Available:** Tables of atomic positional and thermal parameters for **2** (5 pages). Ordering information is given on any current masthead page.

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## State-Selected Mobilities of Atomic Cobalt Ions

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Studies of the reactivities of first row transition metal ions have shown the ion–neutral interaction to be complex and usually extremely dependent on the metal ion electronic state.<sup>1–8</sup> In recent experiments, we have found a striking effect in our measurement of  $\text{Co}^+$  mobility in He. The arrival-time distribution (ATD) for  $\text{Co}^+$  is bimodal, suggesting that two different electronic states are involved with very different interactions with He. This observation is interesting for at least three reasons. First, only one other first row transition metal ion mobility has been measured (ground state  $\text{Ti}^+$ ).<sup>9</sup> Second, our results allow us to perform state-specific chemistry, since known and variable populations of ground- and excited-state ions can be produced and detected.<sup>10</sup> Third, it increases our understanding of  $\text{Co}^+$  reactivity, allowing separation of effects common to all  $\text{Co}^+$ –neutral interactions and those specific to a particular system.

The  $\text{Co}^+$  ions in our experiment<sup>11</sup> are formed by low-pressure electron impact of  $\text{Co}(\text{CO})_3\text{NO}$  (I) and cyclopentadienylcobalt dicarbonyl (II). The ions are mass selected and injected into a high-pressure gas cell. The ions are quickly translationally thermalized by collisions with He ( $P_{\text{He}} \sim 1\text{--}2$  Torr).<sup>11</sup> A small electric field drifts the ions through the cell ( $E/N = 2\text{--}6$  Td). Ions exit the cell and are quadrupole mass analyzed and collected. In the mobility experiments,<sup>11</sup> ions are pulsed into the cell and the

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