Table I. Percentages of Neutral Losses from CID of $RhC_7H_8^+$ Complexes Accelerated to 20-eV Kinetic Energy[a,b]

neutral losses	$Rh(C_7H_8)^+$ [c]	$Rh(CH_3Ph)^+$ [d]	$Rh(c\text{-}C_7H_8)^+$ [d]
H_2	25	28	24
C_2H_2			18
$H_2 + C_6H_6$	57	56	56
C_7H_8	18	16	2

[a] Argon used as target at ~5 × 10^{-6} torr. [b] CID interaction time of 30 ms. [c] $RhC_7H_8^+$ generated from reactions 2 and 3. [d] Generated by displacement of ethylene from $RhC_2H_4^+$ by toluene and cycloheptatriene.

observed.[3] Benzene undergoes a condensation reaction with RhC^+ generating exclusively $RhC_7H_6^+$ (process 5). CID of this product

$$RhC^+ + C_6H_6 \rightarrow RhC_7H_6^+ \qquad (5)$$

yields exclusively RhC^+ with no Rh^+ produced suggesting formation of the carbide–benzene complex **2**. Furthermore, the product of reaction 5 does *not* add hydrogen, clearly eliminating the formation of structure **2** in reaction 1.

CID results indicate that the hydrogenated $RhC_7H_8^+$ products, formed in reactions 2 and 3, have the same structure. In addition their CID spectra are identical (same peaks, intensities, and energy dependence within experimental error) with those for $Rh(CH_3Ph)^+$ formed by ligand displacement reactions and distinguishable from CID of $Rh(c\text{-}C_7H_8)^+$ (Table I). Hence, hydrogenation of $RhC_7H_6^+$ generates formally a $Rh(CH_3Ph)^+$ complex. CID of $RhC_7H_6^+$, generated by reaction 1 with toluene-α-^{13}C, produces $Rh\text{-}^{12}C^+$ and $Rh\text{-}^{13}C^+$ in roughly a 6:1 ratio indicating nearly complete scrambling. This could arise if complexes **1** and **3** are in equilibrium. Lending some support to this possibility is the fact that phenylcarbenes have been found to undergo facile reversible rearrangement to cycloheptatrienylidenes in the gas phase at 250–600 °C[14] and have been treated theoretically.[15] One can rationalize that structure **3** may be undergoing H/D exchanges while hydrogenation of the phenylcarbene complex, **1**, produces the toluene complex.

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Registry No. Rh^+, 20561-59-5; CH_3Ph, 108-88-3.

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Low-Valent Transition-Metal Cyanides: A Crown Ether Strategy for the Development of Their Solution Chemistry

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That cyanide can stabilize the zero oxidation state in transition-metal complexes has been evident for over 40 years.[1,2] However, little is known concerning the reactivity of such complexes. Perhaps the primary barrier to the development of the chemistry of $M(CN)_x^{x-}$ complexes has been their solubility properties. These complexes are isolated as potassium salts, which are completely insoluble in all nonreactive solvents. The same is often true of the ionic reaction products. For example, $K_4Ni(CN)_4$[1] in acetonitrile suspension reacts with PhC≡CPh as evidenced by a color change of the suspended solid. Examination of the product reveals that only a surface layer of $K_4Ni(CN)_4$ has reacted with the acetylene.

We now report a general strategy for dealing with this problem, which has enabled the first synthesis of organonickel cyanides from $K_4Ni(CN)_4$. 18-Crown-6 (**1**) has a profound influence on the course of several chemical reactions involving $K_4Ni(CN)_4$, in spite of its ineffectiveness as a solubilizing agent for $K_4Ni(CN)_4$ in MeCN.[3] Diphenylacetylene (1 equiv) reacts with $K_4Ni(CN)_4$ (1 equiv) in the presence of **1** (2 equiv) with CH_3CN or THF as solvent to give the novel blue-violet complex $(K^+\text{-}\mathbf{1})_2[Ni(CN)_2(PhC{\equiv}CPh)]$ (**2**) (50%) (eq 1). Complex **2** itself does not react with excess PhC≡CPh nor are any organic products evident under the conditions examined thus far. IR and ^1H and ^{13}C NMR data are supportive of an alkyne symmetrically bound to a $Ni(CN)_2^{2-}$ moiety.[4] Compound **2** is the first organometallic complex (excluding carbonyls) to be prepared directly from $K_4Ni(CN)_4$. It is also the first member of the (alkyne)NiL_2 class where L = CN^- and the first anionic member.[5]

$$K_4Ni(CN)_4 + PhC{\equiv}CPh \xrightarrow[CH_3CN,\ 1]{} \underset{\mathbf{2}}{(K^+\text{-}\mathbf{1})_2[Ni(CN)_2(PhC{\equiv}CPh)]} \qquad (1)$$

Efforts to extend this approach to other potential ligands revealed another aspect of the reactivity of $K_4Ni(CN)_4$. While H_2, CO_2, 1,3-butadiene, and 1,5-cyclooctadiene all failed to give evidence of complex formation, consumption of $K_4Ni(CN)_4$ in a slow reaction with MeCN was noted. The nature of this reaction was illuminated by the observation that benzaldehyde reacted under these conditions to give an unexpected product:

$$PhCHO + K_4Ni(CN)_4 + CH_3CN \xrightarrow[CH_3CN,\ 40\%]{1} \underset{\mathbf{3}}{[(\eta^2\text{-}PhCH{=}CHCN)Ni(CN)_2](K\text{-}\mathbf{1})_2} \qquad (2)$$

The spectral evidence for the nature of **3** is straightforward[6a] and closely parallels that for the related $NiL_2(CH_2{=}CHCN)$[6b] and $((E)\text{-}PhCH{=}CHCN)Co(CN)_4^{3-}$[6c] complexes. The identity of **3** is confirmed by the observation that it can be prepared directly from (E)-cinnamonitrile by using the same crown ether method. The apparent implication of reaction 2 is that the $K_4Ni(CN)_4$ + **1** *combination* is a strong enough base to deprotonate acetonitrile (pK_a ~31)[7] to an appreciable extent. By contrast, "normal"

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(1) Eastes, J. W.; Burgess, W. M. *J. Am. Chem. Soc.* **1942**, *64*, 1187–1189.

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(3) Crown ethers have found wide application as solubilizing agents for alkali metal salts in aprotic solvents, but their effectiveness with hydrophilic, polyvalent anions is limited: Montanari, F.; Landini, D.; Rolla, F. *Top. Curr. Chem.* **1982**, *101*, 149-200.

(4) IR (Nujol mull) 2069 (s, $\nu_{C{\equiv}N}$), 2053 (s, $\nu_{C{\equiv}N}$), 1753 (m, br, $\nu_{C{\equiv}C}$), 1731 (m, br, $\nu_{C{\equiv}C}$), 1583 (s, $\nu_{C{=}C(Ph)}$); ^1H NMR (CD_3CN) δ 7.84–6.84 (m, 10 H), 3.60 (s, 48 H); ^{13}C NMR (CD_3CN) δ 140.6 (CN), 137.9 (C≡C), 128.9, 127.6, 123.2, 123.0 (Ph), 70.1 (18-crown-6). Anal. ($C_{40}H_{58}N_2O_{12}$-K_2Ni) C, H, N, Ni.

(5) An analogous reaction occurs with 3-hexyne, but the product has proven to be too unstable to fully characterize although apparently analogous by IR. Reaction with phenylacetylene does not appear to be analogous and as yet has not yielded tractable materials.

(6) (a) IR (Nujol mull) 2161 (s, [C=C]C≡N), 2081 (s, [Ni]C≡N), 2069 (s, [Ni]C≡N), 1590 (s), 1569 (w), ^1H NMR (CD_3CN) δ 6.90 (s, Ph), 3.62 (s, 18-crown-6), 2.68 (d, J = 9.75 Hz, HPhC=), 1.60 (d, J = 9.75 Hz, =C(CN)H); ^{13}C NMR δ 150.6 (NiCN), 128.9, 127.8, 124.1, 119.8 (Ph), 114.1 (nitrile CN), 70.2 (18-crown-6), 40.1 (PhHC=), 25.1 (=C(H)(CN)). (b) Tolman, C. A.; Seidel, W. C. *J. Am. Chem. Soc.* **1974**, *96*, 2774–2780. Tolman, C. A.; English, A. D.; Manzer, L. E. *Inorg. Chem.* **1975**, *14*, 2353–2356. (c) Funabiki, T.; Hosomi, H.; Yoshida, S.; Tarama, K. *J. Am. Chem. Soc.* **1982**, *104*, 1560–1568.

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oxidation state cyanometallates are quite weak bases; e.g., the dissociation constant for $HFe(CN)_6^{3-}$ in water[8] is $\sim 7 \times 10^{-5}$. We see this as clear evidence for the transfer of electron density from the metal to the cyanide ligands via π-backbonding, with a resultant increase in the basicity of the cyanide.

Crown ether mediated reactions of $K_4Ni(CN)_4$ in THF appear to be slow and incomplete although uncomplicated by solvent reactions. The reaction with diphenylacetylene in THF is very slow, yielding only a few percent of product in the time that the same reaction in MeCN goes to completion.[9] Benzaldehyde in THF gives a small amount of a blue-green complex that has so far proven to be too unstable to characterize.

The crown ether strategy permits carrying out in aprotic organic solvents reactions of low-valent cyanonickelates that previously required liquid ammonia as a solvent. Thus reactions of CO with $K_4Ni(CN)_4$[11] or $K_4Ni_2(CN)_6$[12] proceed smoothly in MeCN in the presence of **1**, to give products analogous to those previously obtained; the reaction of $K_4Ni(CN)_4$ + **1** with triphenylphosphine in MeCN also duplicates the literature report.[13]

$$K_4Ni(CN)_4 + XS\ CO + \mathbf{1} \xrightarrow{MeCN} (K\text{-}\mathbf{1})_2Ni(CN)_2(CO)_2 + (K\text{-}\mathbf{1})CN \tag{3}$$

$$K_4Ni_2(CN)_6 + XS\ CO + \mathbf{1} \xrightarrow{MeCN} (K\text{-}\mathbf{1})_2Ni(CN)_2(CO)_2 + (K\text{-}\mathbf{1})_2Ni(CN)_4 \tag{4}$$

$$K_4Ni(CN)_4 + P(C_6H_5)_3 + \mathbf{1} \xrightarrow{MeCN} Ni[P(C_6H_5)_3]_4 \tag{5}$$

These experiments demonstrate the utility of **1** as an efficient solid–liquid phase-transfer reagent for promoting reactions of low-valent nickel cyanide complexes.[14] That the cyanide ligand plays a special role in controlling the reactivity of zerovalent nickel is indicated by the disparate reactivity behavior observed between $K_4Ni(CN)_4$ and isoelectronic $Ni(CO)_4$ toward diphenylacetylene and (*E*)-cinnamonitrile. With $Ni(CO)_4$, which requires more stringent reaction conditions, diphenylacetylene is reported to give hexaphenylbenzene, tetraphenylcyclopentadienone, and bis(tetraphenylcyclopentadienone)nickel(0);[15] cinnamonitile yields the complex bis((*E*)-cinnamonitrile)Ni(0).[16] With a workable methodology now in hand, we are further exploring the chemistry of $K_4Ni(CN)_4$ as well as the new compounds **2** and **3** and their possible applications in synthesis and catalysis. Extension of this synthetic methodology to other transition-metal cyanide systems is possible and will be reported on separately.[17]

Acknowledgment. We thank the Research Corp. for funds for the purchase of a glovebox and the National Science Foundation (Grant CHE-8209006) for support of this research.[18]

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Transition-Metal Cluster Chemistry: Reactions of Mn_2^+ with O_2

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A great deal of attention has recently been focused on the examination of bare metal clusters in the gas phase. Such studies aim to elucidate the intrinsic properties of metal particles in the absence of ligands and solvent. Much of the work to date has concentrated on measurement of the physical properties of clusters.[1,2] The chemistry of metal clusters in the gas phase has received limited attention.[3,4] In a recent publication,[2] we reported on our characterization of the manganese dimer ion using a new ion beam apparatus. In the present study, we extend this work to the chemistry of this cluster with molecular oxygen. This is, to our knowledge, the first observation of reactions of a bare transition-metal cluster in the gas phase.[12]

Experimental details for production and reaction of the manganese dimer ion have been published.[2] Briefly, electron impact ionization and fragmentation of $Mn_2(CO)_{10}$ produces Mn_2^+. By keeping the electron energy close to the appearance potential (18.8 eV)[5] for this ion, we formed the dimer with less than 0.1 eV internal energy.[2] These ions are mass analyzed, formed into a beam of well-defined and easily varied translational energy, and passed through a reaction cell containing O_2. Use of the ion beam guide technique of Teloy and Gerlich[6] keeps product ion collection efficiency high. Product ions are analyzed by a quadrupole mass filter and detected by counting techniques. Although neutral products are not detected directly, they can be determined unambiguously via analysis of the reaction energetics.

Results for the reaction of Mn_2^+ with O_2 are shown in Figure 1. The behavior of the total cross section with relative energy, *E*(CM), is typical for exothermic ion–molecule reactions. Such reactions often exhibit no activation energy due to the strength of the ion-induced dipole potential. At low energies, the experimental cross section decreases as $E^{-0.5\pm0.1}$ as predicted by the

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