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]

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

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

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

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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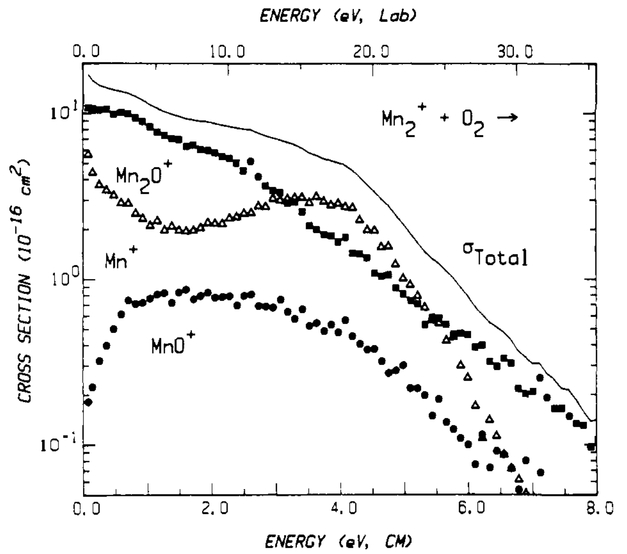

Figure 1. Variation in cross section for reaction of manganese dimer ions with molecular oxygen as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Shown are the cross section for Mn_2O^+ (squares), Mn^+ (triangles), and MnO^+ (circles). The total (solid line) is the sum of the three product cross sections and has been smoothed by using a three point algorithm.

Table I. Thermochemical Data[a]

M	$\Delta H_f{}^\circ{}_0(M)$	IP(M)[b]	$\Delta H_f{}^\circ{}_0(M^+)$
Mn	2.895[c]	7.437	10.332[c]
MnO	1.75 (0.17)[d]	8.1 (0.3)	9.85 (0.25)[e]
		8.65 (0.2)	10.4 (0.1)[f]
MnO_2	−1.5 (1.1)[g]	>7.437[h]	>5.9 (1.1)
Mn_2O			9.4 (0.4)[j]
Mn_2	5.46 (0.30)[k]	6.9 (0.4)	12.38 (0.20)[l]
O	2.558[c]	13.618	16.175[c]
O_2	0[c]	12.071	12.071[c]

[a] All values are in eV. Uncertainties are given in parentheses. IP = ionization potential. [b] Derived from $IP(M) = \Delta H_f{}^\circ{}_0(M^+) - \Delta H_f{}^\circ{}_0(M)$ except where noted. [c] Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data, Suppl.* **1982**, *11*. [d] Cheetam, C. J.; Barrow, R. F. *Adv. High Temp. Chem.* 1967, *1*, 7. [e] Reference 11. [f] Reference 10. [g] Drowart, J.; Goldfinger, P. *Angew. Chem., Int. Ed. Engl.* 1967, *6*, 581–648. [h] This study. [j] Reference 9. [k] Kant, A.; Lin, S.; Strauss, B. *J. Chem. Phys.* 1968, *49*, 1983. [l] Reference 2.

Langevin–Gioumousis–Stevenson model,[7] the close collision limit. The experimental magnitude is 44% of the predicted value indicating that the reaction rate is about half the collision rate. At higher energies, the cross section falls off as $E^{-5.5\pm0.4}$. The smooth behavior of the total cross section belies the extensive structure observed for the three observed product ions. Reactions that can account for these products are processes 1–7. The reaction

$$Mn_2^+ + O_2 \rightarrow Mn_2O^+ + O \qquad +0.4\ (0.4)\ \text{eV} \tag{1}$$

$$Mn_2^+ + O_2 \rightarrow Mn^+ + MnO_2 \qquad +3.5\ (1.1)\ \text{eV} \tag{2}$$

$$Mn_2^+ + O_2 \rightarrow Mn^+ + Mn + O_2 \qquad -0.85\ (0.20)\ \text{eV} \tag{3}$$

$$Mn_2^+ + O_2 \rightarrow Mn^+ + MnO + O \qquad -2.3\ (0.3)\ \text{eV} \tag{4}$$

$$Mn_2^+ + O_2 \rightarrow Mn^+ + Mn + 2O \qquad -6.0\ (0.2)\ \text{eV} \tag{5}$$

$$Mn_2^+ + O_2 \rightarrow MnO^+ + MnO \qquad +0.8\ (0.4)\ \text{eV} \tag{6}$$

$$Mn_2^+ + O_2 \rightarrow MnO^+ + Mn + O \qquad -2.9\ (0.3)\ \text{eV} \tag{7}$$

energetics and uncertainties, given in parentheses, are calculated by using data in Table I. The ions O^+ and O_2^+ are not observed. This is presumably because the ionization potentials (IP) of O and O_2 are much higher than that of any metal-containing species formed concomitantly (Table I).[8]

The most likely process observed, reaction 1, is exothermic as evidenced by the monotonic rise in the cross section with decreasing energy. This reaction is striking since it involves breaking the strong oxygen bond, $D_0°(O_2) = 5.12$ eV, while retaining both metal atoms, $D°(Mn_2^+) = 0.85 \pm 0.20$ eV. The exothermicity of reaction 1 shows that $D°(Mn_2^+\text{–}O) > 5.12$ eV. This is consistent with preliminary results[9] for the dimer ion reaction with CO, which indicate a bond energy of ~5.5 eV. Interestingly, the lowest thermodynamic pathway for decomposition of this ion is to Mn^+ + MnO rather than to Mn_2^+ + O. These processes have energy thresholds of 2.3 ± 0.3 and 5.12 eV, respectively (Table I). Experimentally, only the lowest energy decomposition is apparent. This is noted by the break in the Mn_2O^+ curve at about 2.5 eV.

Atomic Mn^+, the second most likely product, can be formed in reactions 2–5. As can be seen in Figure 1, its cross section has a complex energy behavior exhibiting both an exothermic and endothermic component. The exothermic component must be due to process 2. [Presumably, the competing channel, Mn + MnO_2^+, is not observed because $IP(MnO_2) >> IP(Mn)$.[8]] The endothermic component has a threshold most consistent with reaction 3, the collision-induced dissociation (CID) process. The other possible pathways, reactions 4 and 5, are not immediately obvious due to the complexity of the Mn^+ cross section, but probably do occur at higher energies. For example, reaction 4 can proceed via formation of Mn_2O^+, as noted above.

Production of MnO^+ is apparently endothermic since the cross section clearly shows an energy barrier. However, the threshold is less than 0.1 eV, well below the endothermicity of reaction 7. Thus formation of MnO^+ must occur via the exothermic process, reaction 6. Several possible reasons for the observed activation barrier exist. The origin of the barrier may simply be the competition between process 6 and processes 1 and 2. Especially if tight transition states are involved, diatom–diatom production is more constrained than atom–triatom formation. Spin or orbital symmetry restrictions might also apply; however, this possibility cannot be adequately evaluated due to the lack of information on the electronic states of the ions. At higher energies, the MnO^+ cross section is observed to decrease. This falloff begins near the thermodynamic limit for decomposition of this ion, 2.3 ± 0.3 eV, but is not particularly rapid since the MnO neutral product can also carry away an appreciable amount of energy in internal modes.

The chemistry of the *atomic* manganese ion[10,11] contrasts sharply with the present results. Because the number of atoms involved is less, we expect fewer products and indeed only MnO^+, formed in process 8, is observed. This reaction, the atomic

$$Mn^+ + O_2 \rightarrow MnO^+ + O \tag{8}$$

analogue of reaction 1, is found to be endothermic by about 2.0 eV.[11] Thus, the atomic ion–oxygen bond energy derived from this result, $D°(Mn^+\text{–}O) \sim 3.0$ eV, is nearly half that of the dimer ion, $D°(Mn_2^+\text{–}O) \sim 5.5$ eV.[9] While no structural information can be obtained from these experiments, the bond energy suggests that the oxygen atom interacts strongly with both metal atoms. It will be interesting to see how continued increases in cluster size will affect the general reactivity and thermochemistry of metal systems. Further work in our laboratory is directed at such studies as well as continued examinations of other metals and chemical systems.[12]

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Electron-Transfer Reactions and Luminescent Quantum Yield of the Triplet Excited State of Tetrakis[μ-diphosphito(2−)-*P*,*P'*]diplatinate(II)

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In the short period following the isolation[1] and crystal structure determination[2,3] of $Pt_2(P_2O_5H_2)_4^{4-}$ ($Pt_2(pop)_4^{4-}$), many studies have focused on its intense luminescence[4-11] and the related possibility of metal–metal bonding.[5,6,8,11-15] Although much is now known concerning the detailed nature of the lowest luminescent excited state, only a brief report[6] has appeared describing its photoredox properties. Here we report the results of excited-state electron-transfer quenching studies of $Pt_2(pop)_4^{4-}$ in methanol and also its luminescent quantum yield in aqueous solution. It is demonstrated that the triplet excited state of $Pt_2(pop)_4^{4-}$ is reduced to $Pt_2(pop)_4^{5-}$ by a series of aromatic amine quenchers and shows great promise as a photoredox catalyst.

Quenching studies were performed by standard techniques[16] and analyzed using the Stern–Volmer equation[17] to yield values of k_q, the second-order quenching rate constant. These values are presented in Table I. To correct for diffusion and encounter effects,[18] values of k_q were converted to first-order electron-transfer rate constants k_{et} by $k_{et} = [K(k_q^{-1} - k_d^{-1})]^{-1}$, where k_d is the diffusion rate constant for formation of the encounter complex with equilibrium constant K.[18]

Table I. Rate Constants for Quenching of $Pt_2(pop)_4^{4-*}$ by Aromatic Amines in Methanol Solution at ~25 °C

quencher	$E_{1/2}$, V[a]	k_q, dm^3 mol^{-1} s^{-1} [b]	k_{et}, s^{-1} [c]
N,*N*,*N'*,*N'*-tetramethyl-1,4-benzenediamine, 1	0.11[d]	1.2×10^{10}	6.8×10^{10}
N,*N*,*N'*,*N'*-tetramethyl-[1,1'-biphenyl]-4,4'-diamine, 2	0.36[e]	3.0×10^{9} [i]	2.5×10^{9}
N,*N*,4-trimethylbenzenamine, 3	0.71[f]	3.9×10^{7}	3.2×10^{7}
N,*N*-dimethylbenzenamine, 4	0.78[g]	1.2×10^{7}	1.0×10^{7}
N,*N*-diphenylbenzenamine, 5	0.92[h]	1.5×10^{6}	1.0×10^{6}

[a] Reduction potentials vs. SCE from cyclic voltammetric measurements in room-temperature CH_3CN solutions containing 0.1 dm^3 mol^{-1} tetraalkylammonium perchlorate. Values in CH_3OH are expected to be the same within 0.01 V (Iwa, P.; Steiner, U. E.; Vogelmann, E.; Kramer, H. E. A. *J. Phys. Chem.* 1982, *86*, 1277–1285. Horner, L.; Nickel, H. *Chem. Ber.* 1956, 1681–1690). [b] Second-order quenching rate constants obtained from slopes of Stern–Volmer plots by using $\tau_0 = 7.10 \times 10^{-6}$ s.[17] [c] First-order electron-transfer rate constant for reaction within the encounter pair. See text for explanation. [d] Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* 1980, *102*, 7892–7900. Values of 0.10 V[e] and 0.12 have also been reported. [e] Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* 1981, *103*, 7349–7350. A value of 0.43 V (ref 16 and: Zweig, A.; Maurer, A. H.; Roberts, B. G. *J. Org. Chem.* 1967, *32*, 1322–1329) has also been reported. [f] Reference 16. A value of 0.70 V[d,e] has also been reported. [g] Hino, T.; Akazawa, H.; Masuhara, H.; Mataga, N. *J. Phys. Chem.* 1976, *80*, 33–37. Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* 1978, *100*, 5790–5795. Values of 0.74 V (Jones, P. R.; Drews, M. J.; Johnson, J. K.; Wong, P. S. *Ibid.* 1972, *94*, 4595–4599), 0.79 V (Iwa, P.; Steiner, U. E.; Vogelmann, E.; Kramer, H. E. A. *J. Phys. Chem.* 1982, *86*, 1277–1285), 0.80 V,[16] and 0.81 V[e] have also been reported. The large discrepancy in these values can be partly attributed to the irreversibility of the oxidation using cyclic voltammetry.[16] [h] Debrodt, H.; Heusler, K. E. *Z. Phys. Chem. (Weisbaden)* 1981, *125*, 35–48. Corrected for a reference electrode difference of 0.32 V (Larson, R. C.; Iwamoto, R. T.; Adams, R. N. *Anal. Chim. Acta.* 1961, *25*, 371–374); Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* 1966, *88*, 3498–3503. Values of 0.95 V (Park, S. M.; Bard, A. J. *Ibid.* 1975, *97*, 2978–2985), 1.00 V (Creason, S. C.; Wheeler, J.; Nelson, R. F. *J. Org. Chem.* 1972, *37*, 4440–4446), and 1.06[16] have also been reported. [i] For solubility reasons, 2 was first dissolved in a small amount of acetone and then added to methanol.

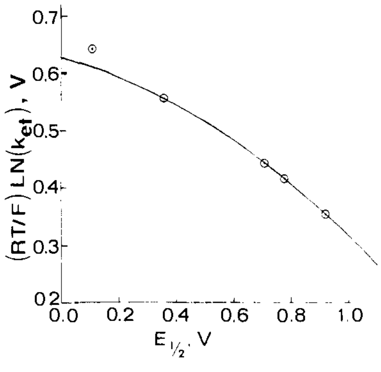

Figure 1. Plot of (RT/F) ln k_{et} vs. $E_{1/2}$ for the quenching of $Pt_2(pop)_4^{4-*}$ by a series of aromatic amines in CH_3OH at ≃25 °C. The solid line corresponds to the best fit of the data to eq 1 assuming $\nu_{et} = 10^{11}$ s^{-1}. See ref 20 for details.

The systematic variation of k_{et} with quencher $E_{1/2}$ values and the high and nearly constant quencher triplet energies[19] supports

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