the desired complex be electrochemically inactive under the electrocrystallization conditions. In addition to the complexes described above, this requirement is met by most charge-transfer complexes since the difference in redox potentials between the individual components, ΔE, is generally positive. That is, neutral donors are usually oxidized at less positive potentials than the acceptor anions, and neutral acceptors are usually reduced at less negative potentials than the donor cations. The observation that crystallization of the moderately soluble charge-transfer complex **1** can be electrochemically induced in saturated solutions illustrates that electrocrystallization is not limited to molecular solids with negligible solubility, as is the case for most one-dimensional conductors formed in "conventional" electrocrystallization[2-6] where presaturation of the medium is not required. Only the degree of solubility is different, and in conventional systems saturation may be reached very quickly due to the negligible solubility of the complexes.

These results demonstrate the generality of electrocrystallization as a convenient technique for the preparation of high-quality crystalline charge-transfer complexes. The ability to precisely control the crystallization process may eventually lead to electronic materials with unique or superior characteristics.

Registry No. **1**, 71035-23-9; **2**, 64679-24-9; **3**, 64679-25-0; $(C_5Me_5)_2Fe$, 12126-50-0; Bu_4N[TCNQ], 34481-16-8; $[(C_6Me_6)_2Ru]$-$[TCNQ]_2$, 104507-52-0; TCNQ, 1518-16-7; $[(C_6Me_6)_2Fe]$[TCNQ], 71357-00-1; $[(C_6Me_6)_2Fe][TCNQ]_4$, 104507-53-1; $[(C_6Me_6)_2Ru]$-$[TCNQ]_4$, 104531-38-6; $[(C_6Me_6)_2Fe][(TCNQ)F_4]_2$, 104507-54-2; $[(C_6Me_6)_2Ru][(TCNQ)F_4]_2$, 104507-55-3; $[(C_6Me_6)_2Fe][(TCNQ)Cl_2]_2$, 104507-57-5; $[(C_6Me_6)_2Ru][(TCNQ)Cl_2]_2$, 104507-58-6.

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Heats of Reaction of $[Mo(CO)_2Cp^*]_2$ ($Cp^* = C_5H_5$, $C_5(CH_3)_5$, C_9H_7) with CO, HC≡CH, and $C_6H_5C≡CH$. Thermochemical Investigation of the Molybdenum-Molybdenum Triple Bond

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The chemistry of complexes that contain formal metal-metal multiple bonds has been the subject of detailed investigations by a number of groups[1] and remains one of the most intriguing areas of transition-metal chemistry. The most widely studied organometallic system is the series of complexes $[M(CO)_2C_5H_5]_2$, where M = Cr, Mo, W.[2] In order to achieve a noble gas configuration, these compounds can be viewed as having a metal-metal triple bond. The carbonyl groups are "semibridging" as shown in Figure 1. Theoretical calculations have suggested that understanding the nature of these dimers does not require postulation of a metal-metal multiple bond.[3]

As part of a program of solution thermochemical study of organometallic complexes, we have reported studies of ligand exchange,[4] hydrogen activation,[5] and carbonyl insertion[6] for the group VI (group 6[26]) metals. We now extend this to an investigation of the complexes $[Mo(CO)_2Cp^*]_2$ ($Cp^* = C_5H_5$, $C_5(CH_3)_5$, C_9H_7).

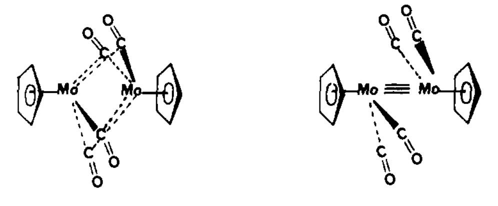

Figure 1. Limiting forms depicting the bonding in $[Mo(CO)_2C_5H_5]_2$. See ref 2c for crystal structure and ref 3 for discussion of the bonding.

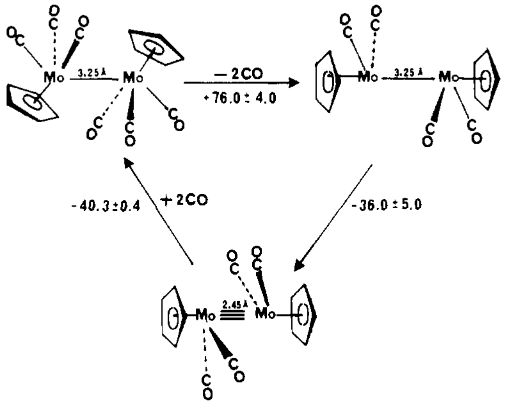

Figure 2. Scheme for estimation of the Mo-Mo interaction in $[Mo(CO)_2C_5H_5]_2$.

Table I. Heats of Reaction and Heats of Solution of $[Mo(CO)_2Cp^*]_2$ Complexes[a]

complex	ligand	ΔH_{exptl}[b]	ΔH_{reacn}[c]
$[Mo(CO)_2C_5H_5]_2$	CO	−36.5 ± 0.3	−40.3 ± 0.4
$[Mo(CO)_2C_5H_5]_2$	HC≡CH	−30.1 ± 1.7	−33.9 ± 1.8
$[Mo(CO)_2C_5H_5]_2$	$C_6H_5C≡CH$	−27.8 ± 0.7	−31.6 ± 0.8
$[Mo(CO)_2C_5(CH_3)_5]_2$	CO	−29.4 ± 0.5	−32.9 ± 0.7
$[Mo(CO)_2C_9H_7]_2$	CO	−26.6 ± 0.7	−31.4 ± 0.7

[a] $Cp^* = C_5H_5$, $C_5(CH_3)_5$, C_9H_7. [b] All values, in kcal/mol, refer to the heat of reaction of the crystalline complex with the excess ligand in toluene solution. Experimental errors are the standard deviation on, typically, five separate determinations. [c] The heat of reaction with all components, in solution, incorporates the experimental values for the heats of solution in toluene of $[Mo(CO)_2C_5H_5]_2$ = +3.8 ± 0.1, $[Mo(CO)_2C_5(CH_3)_5]_2$ = +3.5 ± 0.2 and $[Mo(CO)_2C_9H_7]_2$ = +4.8 ± 0.1 kcal/mol. The heat of solution in THF of $[Mo(CO)_2C_5H_5]_2$ is +2.8 ± 0.2 kcal/mol.

There are three relevant thermodynamic investigations of purely inorganic molybdenum-molybdenum multiple-bonded systems. In the temperature range 2600-3000 K, mass spectrometric investigation of reaction 1 led to a Mo-Mo bond strength estimate of 97 ± 5 kcal/mol.[7] A formal bond order of six has been

$$Mo_2(g) \rightarrow 2Mo(g) \qquad (1)$$

postulated for the diatomic molecule Mo_2.[8] The molybdenum(II) carboxylate $[Mo_2(O_2CR)_4]$ was investigated by solution calori-

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[2] (a) Klinger, R.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1975**, *97*, 3535. (b) King, R. B. *Coord. Chem. Rev.* **1976**, *20*, 155. (c) King, R. B.; Iqbal, M. Z.; King, A. D. *J. Organomet. Chem.* **1979**, *171*, 53. (d) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85. (e) Curtis, M. D.; Klinger, R. J. *J. Organomet. Chem.* **1978**, *161*, 23. (f) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 807. (g) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 802.

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Table II. Molybdenum–Molybdenum Complexes: Bond Lengths, Postulated Bond Orders, and Bond Strength Estimates

complex	Mo–Mo[a]	bond order[b]	bond strength[c]	ref
$[Mo(CO)_3C_5H_5]_2$	3.235	1	32.5	18
$[Mo(CO)_2C_5H_5]_2$	2.448	3	69	this work
$[Mo_2(NMe_2)_6]$	2.214	3	95[d]	11
$[Mo_2(O_2CMe)_4]$	2.093	4	77	9
$[Mo_2](g)$	2.12	6	97	7

[a] Bond lengths are in Å; for original literature references see ref 25. [b] Bond orders listed are those prevalent in the literature relating to these complexes, see discussion for additional details. [c] Bond strength estimates are in kcal/mol. [d] This value is based on the Mo–NMe_2 bond strength for $Mo(NMe_2)_4$, with estimates ranging from 48 to 188 kcal/mol possible in this system; this is the recommended value.[11]

metry. These results suggested a bond strength of 77 kcal/mol in the formally quadruply bonded system.[9] Unlike the case of Mo_2, which is clear-cut, several assumptions about transferability of metal–ligand bond strengths were necessary to elucidate this molybdenum carboxylate system.[10] Finally, solution calorimetric investigation of hexakis(dimethylamido) derivatives of dimolybdenum(III) and ditungsten(III) led to estimates for the molybdenum–molybdenum triple bond in the range 48–188 kcal/mol with a recommended value of 95 kcal/mol.[11] The wide range of values is due to the difficulty in determining which Mo–$N(CH_3)_2$ bond strength estimate to use in the $Mo_2[N(CH_3)_2]_6$ complexes. For all systems, other than the simple diatomic one shown in eq 1, this will be a problem that cannot be resolved by experiment alone.[12] Nevertheless, thermodynamic data for such systems are of real importance in understanding their chemical behavior.

The entryway into the thermochemistry of the $[Mo(CO)_2C_5H_5]_2$ complexes is reaction with CO. This reaction is rapid and quantitative at room temperature.[13] The enthalpy of reaction 2, in toluene solution, is −40.3 ± 0.4 kcal/mol[14] (Table I). This

$$[Mo(CO)_2C_5H_5]_2 + 2CO \rightarrow [Mo(CO)_3C_5H_5]_2 \qquad (2)$$

allows estimation of the metal–metal interaction as shown in Figure 2. Thus the reverse of reaction 2, loss of CO from the single-bonded complex, can be viewed as occurring in the two steps shown in Figure 2. The first involves loss of two terminal carbon monoxide ligands without any change in the geometry of the metal–metal-bonded system. The average value for the Mo–CO bond strength in $Mo(CO)_6$ has been determined as 36 kcal/mol[15] and the first bond dissociation energy as 40.5 kcal/mol, determined by laser pyrolysis.[16] Adopting an average value of 38 ± 2 kcal/mol implies that the energy required to dissociate 2 mol of CO in the first step in Figure 2 should be 76 ± 4 kcal/mol. Since the overall reaction is endothermic by 40.3 kcal/mol, then the transformation in the second step, collapse of the structure to the triple-bonded geometry, is calculated to be exothermic by 36 kcal/mol. Due to experimental errors and uncertainty in the Mo–CO bond strength, we consider this value accurate to within 5 kcal/mol.[17] This result is independent of the nature of the interaction between the metal centers and cannot resolve whether this energy is due to a pure metal–metal bond or involves only the interaction with the semibridging carbonyls or some admix of both. For the sake of simplicity, we refer to this as the molybdenum–molybdenum triple bond, and indeed this simple interpretation appears most reasonable. Kinetic data have been used to estimate the single-bond energy in $[Mo(CO)_3C_5H_5]_2$ as 32.5 ± 0.5 kcal/mol.[18] Thermochemical investigations in our laboratory corroborate this result.[3e,f] This leads to an estimation of the Mo–Mo triple bond as 69 ± 5.5 kcal/mol. Included in Table II is a summary of bond lengths, postulated bond orders, and estimated bond strengths for several molybdenum–molybdenum-bonded complexes.

The heat of addition of carbon monoxide to the permethylated derivative $[Mo(CO)_2C_5(CH_3)_5]_2$ is −32.9 ± 0.7 kcal/mol, and to the η^5-indenyl complex $[Mo(CO)_2C_9H_7]_2$[19] it is −31.4 ± 0.7 kcal/mol. The reduced stability of the single-bonded relative to the triple-bonded complex for these ligands is probably due to steric factors. Thus, incorporation of additional CO is most favored for the unsubstituted cyclopentadienyl derivative. Nevertheless, the possible contribution of electronic factors cannot be excluded.

Finally, we have measured the heats of addition of acetylene, and phenylacetylene to $[Mo(CO)_2C_5H_5]_2$, as shown in eq 3. The

$$[Mo(CO)_2C_5H_5]_2 + RC{\equiv}CH \rightarrow [\mu\text{-}RC{\equiv}CH][Mo(CO)_2C_5H_5]_2 \qquad (3)$$

enthalpies of these reactions in solution were −33.9 ± 2.0 and −31.6 ± 1.5 kcal/mol for acetylene and phenylacetylene respectively.[20] These values indicate a strong interaction between the dinuclear center and the bridging acetylene, nearly equal to that of 2 mol of CO. Recent work in our laboratory has shown that olefins and dienes form relatively weak bonds, some 14 kcal/mol weaker than that of CO based on individual bond strengths.[21] Thus, if the acetylene bond were modeled by a diene, the estimated heat of addition to the triple-bonded dimer would be some 28 kcal/mol less than the heat of addition of CO, whereas it is actually only about 6 kcal/mol less. The crystal structure determinations of the acetylene complexes[22] show considerable distortion of the organic ligand. Investigation of mononuclear acetylene complexes is planned in order to determine if the stability of the bridging dinuclear acetylene complexes is due to the metal–acetylene bond being inherently stronger than the metal–diene bond, or if the unexpectedly high value for the heat of binding of acetylenes is due to the unique character of the bridging structure.

Examination of the data in Table II leads to the conclusion that the metal–metal interaction is not particularly strong in these systems. The fact that reaction 2 occurs guarantees this. Reasonable estimates about the entropy of reaction 2 limit the metal–metal triple bond to some 60 kcal/mol higher than the

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(9) Cavell, K. J.; Garner, C. D.; Pilcher, G.; Parkes, S. *J. Chem. Soc., Dalton Trans.* **1979**, 1714.

(10) For an excellent discussion of this point see ref 11b,c.

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(12) For any complex other than $M_2(g)$ this will be a problem. Thus while it may be possible to obtain an accurate estimate for the enthalpy of the reaction

$$[M_2(L)_n] \rightarrow 2[M(L)_n]$$

detailed interpretation of this enthalpy will require a theoretical justification of the partitioning of energy in this process. Even for nonbridging ligands it can not be assumed that the M–L bond strengths in the two fragments are the same. Ultimately the net energy of this process is of importance regardless of whether theoretical interpretation shows it to reside in the metal–metal or metal–ligand bonds.

(13) Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 3533.

(14) In a typical experiment a sealed ampule containing 0.15 g of the organomolybdenum complex was broken in a solution of 400 mL of freshly distilled toluene saturated with purified carbon monoxide in a calorimeter system that has been described previously.[4–6]

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(16) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

(17) This refers to the error in estimation of the transformation of the second step in Figure 2, which incorporates an error of 4 kcal/mol in the estimate of the Mo–CO bond strength contribution plus an experimental error of 0.4 kcal/mol.

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(19) Greaney, M. A.; Merola, J. S.; Halbert, T. R. *Organometallics* **1985**, *48* 2057.

(20) At room temperature we did not find evidence for addition of phenylacetylene to $[Mo(CO)_2C_5(CH_3)_5]_2$ and so we could only measure the heat of reaction of the unsubstituted cyclopentadienyl complex.

(21) For example one-third of the bond strength for the triolefin cycloheptatriene in the complex $CHPTMo(CO)_3$ is 24 kcal/mol,[4b] a value that presumably reflects the individual Mo–olefin bond strength. This value is virtually identical with half of the value for the bond strength estimate for the diolefin norbornadiene in the complex $(NBD)Mo(CO)_4$.[4f]

(22) Bailey, W. I.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5764.

single bond.[23] There is no simple relationship between bond length and bond strength. Nevertheless, the rough correlation in Table II gives confidence to these data since each of the compounds was studied by different groups using different techniques. A recent theoretical study of Mo_2H_6 predicts a value for the Mo–Mo triple-bond strength of 68 kcal/mol,[24] in surprising agreement with our work. Additional thermochemical investigations on these and related complexes are in progress, and it is hoped that this work will provide a basis for practical and theoretical understanding of the chemistry of this important class of compounds.

Acknowledgment. Support of this work by the National Science Foundation (Grant No. CHE-8314497) is gratefully acknowledged.

Registry No. $[Mo(CO)_2C_5H_5]_2$, 56200-27-2; $[Mo(CO)_2C_5(CH_3)_5]_2$, 12132-04-6; $[Mo(CO)_2C_9H_7]_2$, 98540-88-6; CO, 630-08-0; $HC{\equiv}CH$, 74-86-2; $PhC{\equiv}CH$, 536-74-3.

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(23) (a) A recent estimate for the loss of translational and rotational entropy in uptake of 1 mol of CO(g) is 36 eu.[23b] Thus there is a net unfavorable entropy change associated with reaction 2 of roughly 72 eu, which results in a $T\Delta S$ term of 21.5 kcal/mol opposing addition of CO to the triple-bonded dimer. For CO addition to occur at all the enthalpy of reaction 2 must be at least −21.5 kcal/mol to offset the entropy term. Considering the maximum gain in energy by addition of two terminal CO ligands to be 80 kcal/mol implies that a loss of metal–metal bond energy of more than 58.5 kcal/mol would lead to a net unfavorable free energy for addition of CO. (b) Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J. B.; El Saied, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics*, **1981**, *1*, 1166.

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(26) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Convenient Synthetic Route to Coordination and Organometallic Compounds of Alkanenitronate $[O_2N{=}CRR']^-$ Anions[1]

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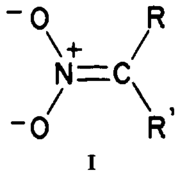
Nitronate anions (I) represent a potentially useful class of bidentate ligands whose coordination chemistry has been little studied. Numerous studies exist on the coordination chemistry of related nitrito and nitrato ligands—anions that exhibit N-bonded, monodentate O-bonded, chelating O-bonded, and bridging coordination modes.[2] Related to both of these ions are the alkanenitronato ligand, derived conveniently via base deprotonation of the corresponding nitroalkane.



I

The importance of aliphatic nitro compounds in the interconversion of organic functional groups has long been appreciated,[3] and recent attention has focused increasingly on the chemistry of mono- and dianions derived from such nitro compounds.[4] Our interest in such molecular fragments centers on (i) the potential for modification of reactivity of such anions via prior coordination and (ii) the possibility of diastereofacial selectivity in subsequent inter- and intramolecular reactions at the alkanenitronate moiety.

Recent reports demonstrate clearly the ability of alkanenitronate anions to bind in a symmetrically chelating fashion: synthetic approaches to such coordination complexes have required (i) the reactions of arylcopper(I) complexes, in the presence of phosphine base, with nitroalkanes (with concomitant loss of arene) to afford Cu(I)–nitronate species[5] and (ii) reaction of the nitronate anion, generated via sodium hydroxide deprotonation, in aqueous solutions of Ni(II) to yield a bis(nitronato)nickel(II) species.[6] We sought a more direct and potentially more generally applicable route to such compounds. Our approach involves the reaction, under nonaqueous conditions, of the appropriate nitroalkane anion with a metal halide. The alkanenitronate reagent employed may be a conveniently weighable free-flowing solid, or the anion may be generated in situ and reacted subsequently with the metal halide without prior isolation.

We report herein the preparation and characterization of a series of new $Cp_2Zr(X)(O_2N{=}CRR')$ (X = Cl^- or alkyl, R, R′ = H or Me) complexes and the homoleptic, eight-coordinate $Zr[O_2N{=}C(CH_3)_2]_4$. In addition, one of these Cp_2ZrL_3 systems has been characterized via X-ray crystallography to substantiate the mode of coordination.

Experimental Section

All procedures were performed under nitrogen in Schlenk-type glassware with normal bench-top Schlenk techniques.[7] Manipulations involving O_2- and/or H_2O-sensitive solids were accomplished conveniently in an Ar-filled glovebox (Vacuum Atmospheres). Argon and nitrogen were purified by passage through a supported MnO oxygen removal column[8] and a Linde 4-Å molecular sieve column. Cp_2ZrCl_2 (Aldrich) was used as received while $ZrCl_4$ (Alfa) was sublimed prior to use and stored in the glovebox. Nitroethane and nitropropane (Aldrich) were refluxed over and distilled from phosphorus pentoxide under a nitrogen atmosphere and stored over molecular sieves under a nitrogen atmo-

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(1) Presented in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 8–13, 1985; Abstract No. 383. A more systematic name for an alkanenitronate would be as a derivative of an *N*-hydroxy imine *N*-oxide.

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