molar entropy on forming highly charged activated complexes.

Values for $\Delta H^{\ddagger}_{RuRu} = 10.3$ kcal/mol and $\Delta H^{\ddagger}_{VV} = E_a - RT = 12.6$ kcal/mol have been reported.[16,17] (While previous reservations regarding the vanadium value remain in effect, the outer-sphere $\Delta H^{\ddagger}_{VV}$ at $I = 0.10$ is not likely to be greatly different.) A ΔH°_{VRu} of -20.6 kcal/mol can be estimated from reduction potentials given below and ΔS°_{VRu}, again assuming applicability to our conditions. The low $\Delta H^{\ddagger}_{VRu}$ appears understandable then in terms of a ~ 10-kcal combined self-exchange contribution which is compensated by an almost equal counter contribution from ΔH°_{VRu}. In terms of the absolute Marcus theory[1-3] the molecular source would appear to reside primarily in a first-coordination-sphere (or outer-sphere) rearrangement barrier which has been diminished relative to the self-exchange reactions, as a result of the ground-state difference in redox orbital energies which is also reflected in the favorable net potenial. (This represents an extension of previous analyses.)[20,21]

Finally, we have calculated an unambiguously outer-sphere, *apparent* self-exchange rate for the vanadium couple under our conditions ($I = 0.10$) from[1,3]

$$\log k_{VV} = 2 \log k_{VRu} - \log k_{RuRu} - \frac{\Delta E^{\circ}}{0.059} - \log f$$

where $\log k_{RuRu}$ and $E^{\circ}_{1/2}(Ru)$ are estimated at $I = 0.10$ as 3.5 and 0.078 V, respectively, from data at other ionic strengths;[19] $E^{\circ}_{1/2} = -0.255$ V for the vanadium couple;[22] and $\log f = -0.4$. The resulting value for k_{VV} of 3×10^{-3} M^{-1} sec^{-1} (1.1×10^{-3} if the $\log f$ term is ignored) seems more appropriate for use in the Marcus theory context at $I = 0.10$ than the value of 1×10^{-2} M^{-1} sec^{-1} obtained at $I = 2.0$.[19]

Registry No. $V(H_2O)_6{}^{2+}$, 15696-18-1; $Ru(NH_3)_6{}^{3+}$, 18943-33-4.

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Alternate Routes to the $Mo_2Cl_9{}^{3-}$ and $Mo_2Br_9{}^{3-}$ Anions

W. H. Delphin and R. A. D. Wentworth*

The preparation of the anion $Mo_2X_9{}^{3-}$ (X = Cl or Br) has been achieved by several different routes: (1) the reaction of MoX_3 and CsX in a sealed tube at about 800°;[1] (2) the electrolytic oxidation of $Mo_2Cl_8{}^{3-}$ in aqueous HCl solu-

tions;[2] (3) the addition of alkylammonium or alkali metal halides to aqueous HX solutions of Mo(III);[3] and (4) the oxidative displacement of CO from $Mo(CO)_4Cl_3{}^-$ by $MoCl_6{}^{2-}$ in CH_2Cl_2 solutions.[4] The last reaction, which was designed specifically to achieve the desired synthesis, is typified by a change in the oxidation state of each reacting metal atom such that the oxidation states of the metal atoms in the product are identical, *i.e.*, +3. Other examples of this kind of reaction are the preparations of WCl_4 and WCl_5 by the reaction of stoichiometric proportions of WCl_6 and $W(CO)_6$ and $MoCl_4$ from $MoCl_5$ and $Mo(CO)_6$.[5] We have continued to investigate reactions such as these in order to determine their utility in the preparation of polynuclear halomolybdates. We report in this paper the following successful reactions conducted in CH_2Cl_2 solutions.

$$6MoCl_5 + 4Mo(CO)_5Cl^- + 11Cl^- \rightarrow 5Mo_2Cl_9{}^{3-} + 20CO \qquad (1)$$

$$3MoBr_4 + Mo(CO)_5Br^- + 5Br^- \rightarrow 2Mo_2Br_9{}^{3-} + 5CO \qquad (2)$$
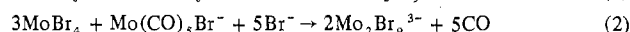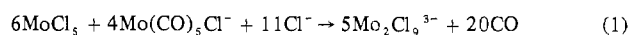
Reaction 1 gave $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$ in high yield (83%), but difficulties encountered in working up an alkylammonium salt of $Mo_2Br_9{}^{3-}$ probably account, at least in part, for the lower yield (54%) obtained from reaction 2.

These reactions demonstrate the scope and utility of the method since the expected products could be obtained starting with either Mo(IV) or Mo(V) halides and suitable adjustment of the stoichiometry of the reactants. These oxidation-reduction reactions are undoubtedly driven by the release of CO. However, each probably proceeds through a complex series of intermediates and no mechanistic interpretation will be attempted. It is noteworthy that attempts to produce $MoCl_6{}^{3-}$ by increasing the proportion of Cl^- in reaction 1 failed since the product was again $Mo_2Cl_9{}^{3-}$.

Experimental Section

Reagents and Procedures. Samples of $MoCl_5$ were prepared by halogenation of the metal.[6] The preparation of $MoBr_4$ was accomplished by exhaustive bromination (2 hr at room temperature) of $Mo(CO)_6$ in the absence of a solvent.[7] Alkylammonium salts of $Mo(CO)_5X^-$ (X = Cl or Br) were prepared by the reaction of the halide with $Mo(CO)_6$.[8] The reactions which follow were conducted under conditions previously described.[9] The compounds which were isolated from these reactions were always washed with the cold distillate from the mother liquor and dried under vacuum.

Preparation of Compounds. $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$. A solution of $[(n\text{-}C_4H_9)_4N]Mo(CO)_5Cl$ (1.67 mmol) and $[(n\text{-}C_4H_9)_4N]Cl$ (4.76 mmol) was prepared in CH_2Cl_2 (~40 ml). Solid $MoCl_5$ (2.51 mmol) was then added to this solution. After 38 hr evolution of CO had ceased with a total of 6.00 mmol (72%) measured. The solution was filtered yielding $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$ (0.68 mmol). *Anal.* Calcd for $C_{48}H_{108}N_3Mo_2Cl_9$: Mo, 15.5; Cl, 25.8. Found: Mo, 15.8; Cl, 25.6. The filtrate was diluted to 50.0 ml and aliquots of this solution were used for quantitative spectroscopic analyses. An infrared spectrum indicated that the only CO-containing species was $Mo(CO)_6$ (0.28 mmol). The only chromophoric species evident in the visible spectrum was $Mo_2Cl_9{}^{3-}$ (1.06 mmol). The total yield of $[(n\text{-}C_4H_9)_4N]_3Mo_2Cl_9$ was 83% (1.74 mmol).

$[(n\text{-}C_4H_9)_4N]_3Mo_2Br_9$. A freshly prepared sample of $MoBr_4$

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(4.05 mmol) was mixed with $[(n\text{-}C_4H_9)_4N]Mo(CO)_5Br$ (1.33 mmol). Upon addition of a solution of CH_2Cl_2 (~40 ml) containing $[(n\text{-}C_4H_9)_4N]Br$ (6.73 mmol), a reaction began with vigorous evolution of CO. After 24 hr CO evolution ceased with a total of 5.86 mmol of CO evolved (88%). Attempts to isolate the $[(n\text{-}C_4H_9)_4N]^+$ salt resulted in oils; however, the $[(n\text{-}C_3H_7)_4N]^+$ salt was isolated by adding the solution to a solution of 1.8 g of $[(n\text{-}C_3H_7)_4N]Br$ in 20 ml of CH_2Cl_2. The product (1.44 mmol) precipitated immediately as a red powder. Recrystallization was accomplished by the slow addition of ether to a solution of the salt in CH_3CN. *Anal.* Calcd for $C_{36}H_{84}N_3Mo_2Br_9$: Mo, 13.0; Br, 49.0. Found: Mo, 13.0; Br, 48.5.

Contribution from the Department of Chemistry,
University of California, and Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720,
and the Department of Chemistry, Indiana University,
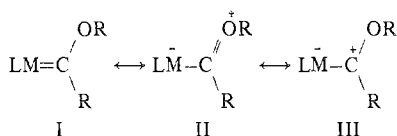Bloomington, Indiana 47401

Determination of the Electron Distribution in a Transition Metal Carbene Complex by X-Ray Photoelectron Spectroscopy

Winfield B. Perry, Theodore F. Schaaf, William L. Jolly,*
Lee J. Todd, and David L. Cronin

There is much current interest in the structure and bonding of transition metal carbene complexes.[1,2] A carbene complex in which the carbene carbon atom is bonded to a heteroatom with nonbonding electrons, such as LMC(OR)R, may be represented as a resonance hybrid of structures I–III.

$$\underset{\text{I}}{\overset{\overset{\displaystyle OR}{/}}{LM=C}\overset{\displaystyle }{\underset{\displaystyle\backslash}{}}R} \quad\longleftrightarrow\quad \underset{\text{II}}{\overset{\overset{\displaystyle\overset{+}{O}R}{\|}}{\bar{LM}-C}\overset{\displaystyle }{\underset{\displaystyle\backslash}{}}R} \quad\longleftrightarrow\quad \underset{\text{III}}{\overset{\overset{\displaystyle OR}{/}}{\bar{LM}-\overset{+}{C}}\overset{\displaystyle }{\underset{\displaystyle\backslash}{}}R}$$

Recent carbon-13 nmr data have been interpreted as evidence for electron deficiency in the carbene carbon and for characterization of such compounds as "transition metal stabilized carbonium ions."[3,4] Davison and Reger[5] have pointed out that the reactivity patterns of the compounds warrant their description as "carboxonium rather than carbenoid compounds." Cardin, *et al.*,[1] discussed other physical and chemical data which have been interpreted as evidence that II and III are the principal contributing structures. In view of the current interest in the charge distribution in such complexes,

* Address correspondence to this author at the University of California.

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Table I. Relative Core Binding Energies and Calculated Atomic Charges

Compd and atom[a]	Rel E_B, eV Exptl	Rel E_B, eV Calcd[b]	Calcd[b] charge
$Cr(\overset{*}{C}O)_6$	0.0	0.0	0.20
$(\overset{*}{C}O)_5CrC(OCH_3)CH_3$	−0.7	−0.6	0.19
$(CO)_5Cr\overset{*}{C}(OCH_3)CH_3$	−2.7[c]	−2.3	0.11
$(CO)_5CrC(O\overset{*}{C}H_3)CH_3$	−1.4[c]	−0.1	0.10
$(CO)_5CrC(OCH_3)\overset{*}{C}H_3$	−1.4[c]	−1.9	0.01
$Cr(\overset{*}{C}O)_6$	0.0	0.0	−0.03
$(\overset{*}{C}O)_5CrC(OCH_3)CH_3$	−0.8[d]	−0.3	−0.03
$(CO)_5CrC(\overset{*}{O}CH_3)CH_3$	−0.8[d]	−2.1	−0.14
$\overset{*}{C}rO_2Cl_2$	0.0	0.0	0.92
$\overset{*}{C}r(CO)_6$	−5.4	−5.5	−1.02
$(CO)_5\overset{*}{C}rC(OCH_3)CH_3$	−6.2	−6.1	−1.02

[a] Asterisked atoms correspond to the listed binding energies and charges. [b] Calculated for a hybrid structure (see text). [c] These values are relatively uncertain; they are based on a computer resolution of the C 1s band (see text). [d] A single O 1s peak was observed.

we have used X-ray photoelectron spectroscopy[6,7] to determine the relative importance of the resonance structures in methoxy(methyl)carbenepentacarbonylchromium(0), $(CO)_5\text{-}CrC(OCH_3)CH_3$.[8] This complex has sufficient volatility at room temperature so that we could study it as a gas and avoid the problems associated with solid-state spectra.

Experimental Section

Spectra were obtained with the Berkeley iron-free magnetic-focusing spectrometer using Mg $K\alpha_{1,2}$ X-rays.[9] Argon $[E_B(2p_{3/2}) = 248.45$ eV] was introduced as a standard reference with each sample. The $(CO)_5CrC(OCH_3)CH_3$ was prepared by the method of Fischer and Maasbol;[8] the $Cr(CO)_6$ was purchased; the CrO_2Cl_2 was prepared by the reaction of sodium dichromate with hydrochloric acid.[10] In Table I are listed the carbon 1s, oxygen 1s, and chromium $2p_{3/2}$ binding energies relative to the values $E_B(C 1s) = 293.11$ eV and $E_B(O 1s) = 539.96$ eV for $Cr(CO)_6$ and $E_B(Cr 2p_{3/2}) = 587.64$ eV for CrO_2Cl_2.

Results and Discussion

The carbon 1s spectrum is shown in Figure 1. The only features due to pure core ionization are the peak at 292.37 eV and its low binding energy shoulder. Undoubtedly the main peak is principally due to the five carbonyl carbon atoms. The shoulder and perhaps part of the intensity of the main peak are due to the other three carbon atoms. To provide an objective analysis of this portion of the spectrum, we have resolved the band by a least-squares curve-fitting routine into four peaks with an enforced intensity ratio of 5:1:1:1. This analysis placed the intense peak at 292.37 ± 0.10 eV and the weak peaks at 291.7 ± 0.3, 291.7 ± 0.3, and 290.4 ± 0.3 eV. Although the latter three binding energies are not to be taken very seriously, the analysis does show that the binding energies of the weaker components of this band are lower than that of the intense carbonyl component.

The band with a binding energy 5.4 eV higher than that of the main peak, with an intensity 0.18 times that of the main peak, is similar to a band observed in the oxygen 1s spec-

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