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# Rates of Halogen Atom Transfer to Manganese Carbonyl Radicals[†,1]

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Flash photogeneration of $Mn(CO)_4L\cdot$ radicals (L = CO, L) from 1,2-diax-$Mn_2(CO)_8L_2$ in the presence of organic halides, or physical mixing of $Mn(CO)_3L_2\cdot$ (L = $PR_3$) and organic halide solutions, produces $Mn(CO)_{5-y}L_yX$ as the only product. Bimolecular atom transfer rate constants, $k_T$, were measured for several radical/halide pairs by monitoring the decay of the visible or infrared absorbance of the radical. The rate constants vary over a range of $10^{10}$. Both the phosphine and organic halide affect the magnitude of $k_T$. The rate of halogen atom transfer is accelerated by increased electron density at the metal center and is impeded by phosphine ligand bulk, as measured by the cone angle. The rate constants for reaction of $CCl_4$ with $Mn(CO)_3[P(i\text{-}Bu)_3]_2$ or $Mn(CO)_3[P(i\text{-}Pr)_3]_2$ are smaller than for reaction with $Mn(CO)_4P(i\text{-}Bu)_3$ or $Mn(CO)_4P(i\text{-}Pr)_3$, respectively. For a given halogen X, the rate constant is faster for C–X bonds of lower bond dissociation energy.

## Introduction

There has recently been much interest in the photogeneration of organometallic radicals in solution at room temperature. Various unbridged metal carbonyl dimers including $[CpM(CO)_3]_2$[2,3] (Cp = $\eta^5$-$C_5H_5$; M = Mo, W) and $M_2(CO)_{10}$[2,4,5] (M = Mn, Re) are known to undergo efficient homolytic metal–metal bond cleavage following irradiation at wavelengths corresponding to a $\sigma \rightarrow \sigma^*$ or $d\pi \rightarrow \sigma^*$ transition (eq 1). Radical formation by flash photolysis[3,6-10] or pulse radiolysis[11,12] allows measurement of the electronic absorption spectrum of the transients and kinetics measurements of their rates of recombination. Bimolecular recombination rate constants, $k_r$, approaching the diffusion-controlled limit are observed for many of these radicals.[3,6-9,11,12]

$$L_z(CO)_yM\text{–}M(CO)_yL_z \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} 2M(CO)_yL_z\cdot \qquad (1)$$

The radicals, once formed, are capable of reaction by a variety of pathways including recombination, ligand substitution,[5,13,14] oxidation,[15] and atom transfer reactions[3,5,9,12,15,16] as illustrated by the examples in eq 2–5.

$$2Mn(CO)_5\cdot \rightarrow Mn_2(CO)_{10} \qquad (2)$$

$$Mn(CO)_5\cdot \xrightarrow{PPh_3} Mn(CO)_4PPh_3\cdot \qquad (3)$$

$$CpW(CO)_3\cdot \xrightarrow[CH_3CN]{[Cp_2Fe]^+} [CpW(CO)_3(CH_3CN)]^+ \qquad (4)$$

$$Re(CO)_5\cdot \xrightarrow{CCl_4} Re(CO)_5Cl \qquad (5)$$

Halogen atom transfer from organic halides to metal-centered radicals was initially employed[3,5] along with cross-coupling reactions[5,17] to demonstrate that photolytic metal–metal bond cleavage is homolytic.

More quantitative experiments have been recently reported. The rate of chlorine atom transfer from organic halides to $CpW(CO)_3\cdot$ was estimated by Laine and Ford on the basis of quantum yield determinations and competition experiments.[18] The bimolecular atom transfer rate constant $k_T$ varied from $1.3 \times 10^4$ $M^{-1}$ $s^{-1}$ for $CCl_4$ to 0.6 $M^{-1}$ $s^{-1}$ or less for $CH_2Cl_2$. Abrahamson and Wrighton determined the relative reactivities of several 17-electron radicals by photolyzing various mixed-metal dimers in the presence of 1-iodopentane or $CCl_4$ and measuring the relative amounts of each product.[19] Hepp and Wrighton have also reported the ratio of the rates of atom transfer vs. oxidation for various radicals in the presence of several pairs of organic halides and oxidizing agents in different solvents.[15] They conclude that atom transfer does proceed by direct transfer of a halogen atom, as opposed to an alternative pathway involving halide ion transfer followed by back-electron transfer. Only a few direct measurements of halogen atom transfer rate constants have been reported. Wojcicki and co-workers observed that $Re(CO)_5\cdot$ and $Mn(CO)_5\cdot$ abstract chlorine from $CCl_4$ in ethanol, with bimolecular atom transfer rate constants of $3.9 \times 10^7$ and $6.1 \times 10^5$ $M^{-1}$ $s^{-1}$, respectively.[12] Yasufuki and co-workers measured a rate constant of $9.1 \times 10^5$ $M^{-1}$ $s^{-1}$ for chlorine atom transfer from $CCl_4$ to $Mn(CO)_5\cdot$ in neat $CCl_4$.[9]

To assess the importance of thermodynamic, electronic, and steric effects on halogen atom transfer, we have measured the rates of atom transfer from several organic bromides and chlorides to the manganese carbonyl radicals $Mn(CO)_5\cdot$, $Mn(CO)_4PR_3\cdot$, and $Mn(CO)_3(PR_3)_2\cdot$. Both $Mn(CO)_5\cdot$ and $Mn(CO)_4PR_3\cdot$ radicals were generated in the presence of an organic halide by using xenon lamp or laser

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[†] Dedicated to the memory of Earl L. Muetterties.

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[2] Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246.

[3] Hughey, J. L.; Bock, C. B.; Meyer, T. J. *J. Chem. Soc.* **1975**, *97*, 4440.

[4] Freeman, A.; Bersohn, R. *J. Am. Chem. Soc.* **1978**, *100*, 4116.

[5] Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

[6] Hughey, J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49.

[7] Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089.

[8] Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.*, in press.

[9] Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakuru, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249.

[10] Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536.

[11] Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259.

[12] Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 1842.

[13] (a) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095. (b) Fox, A.; Malito, J.; Poe, A. *J. Am. Chem. Soc.* **1981**, *103*, 1052.

[14] McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007.

[15] Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258.

[16] McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496.

[17] Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822.

[18] Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388.

[19] Abrahamson, H. B.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 5510.

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flash photolysis. The reactions were monitored by following the disappearance of the absorbance in the visible absorption spectrum due to the radical. Rates of reaction of the persistent radicals $Mn(CO)_3(PR_3)_2\cdot$ were followed by using stopped-flow techniques; reaction rates were monitored by using IR.

## Experimental Section

**Materials.** $Mn_2(CO)_{10}$ was purchased from Pressure Chemical Co. and sublimed before use. Phosphines were obtained from Strem Chemical Co. Tri-*n*-butylphosphine, triisobutylphosphine, and triisopropylphosphine were distilled from $CaH_2$ under reduced pressure of $N_2$ for use in the preparation of persistent radicals. Organic halides were purchased from standard sources. $CBr_4$ was recrystallized from ethanol, washed, and dried in vacuo overnight. $CHBr_3$, $CH_2Br_2$, and $CHCl_3$ were purifed by consecutive treatment with $H_2SO_4/H_2O/NaOH$(dilute)$/H_2O/CaCl_2$ before distillation from $P_2O_5$. $CHBr_3$ and $CHCl_3$ were distilled at reduced pressure. Benzyl bromide and benzyl chloride were washed with $H_2O$, dried over $CaCl_2$, and distilled under reduced pressure. $CCl_4$ was washed consecutively with hot concentrated alcoholic KOH(3 times)/$H_2O/CaCl_2$ and distilled from $P_2O_5$. The collected distillates were placed in amber bottles and degassed with an argon purge. The halide reagents were stored in the drybox. Hexane was purified by consecutive treatment with $H_2SO_4/H_2O$/aqueous $NaHCO_3/H_2O/MgSO_4$ prior to distillation from $CaH_2$. Argon (NGC Industrial Gases, 99.998%) was used without further purification.

$Mn_2(CO)_8L_2$ (L = $P(n\text{-}Bu)_3$, $P(i\text{-}Bu)_3$, $P(i\text{-}Pr)_3$, $P(C_6H_{11})_3$, $P(O\text{-}i\text{-}Pr)_3$)[6,7] and $Mn(CO)_3L_2\cdot$ (L = $P(n\text{-}Bu)_3$, $P(i\text{-}Bu)_3$, $P(i\text{-}Pr)_3$)[16] were prepared by using standard procedures. $Mn_2(CO)_8[P(C_6H_{11})_3]_2$ ($C_6H_{11}$ = cyclohexyl) has not been reported previously. It has the normal 1,2-diaxial geometry as judged by infrared spectroscopy: IR (hexane) $\nu$(CO) 1953 $cm^{-1}$.

**Kinetics Techniques.** The flash photolysis,[8] long time scale stopped-flow,[16] and short time scale stopped-flow[20] apparatuses have been described previously. The laser flash photolysis system consisted of a Molectron UV-24 $N_2$ laser (337 nm, 10-ns fwhm, 900-kW peak power), excitation source, and a 450-W Xe lamp monitoring source that could be operated in the pulsed or continuous modes. The light sources are in a perpendicular arrangement. Filters (cutoff between 600 and 700 nm) between the xenon lamp and the cell remove higher energy photons from the monitoring beam. An Instruments SA, Inc., Model H-20 monochromator with IR grating (300–1100 nm) and a Hammamatsu R928 photomultiplier tube (peak response 400 nm) complete the optical train. The Tektronix 512 channel 8 bit digitizer accumulated the data, which was later stored on disk. The data are transferred to a VAX 11/780 computer for analysis.

Samples for flash photolysis and laser flash photolysis were prepared in the drybox and loaded in appropriate cells with threaded Teflon stopcocks. Sample solutions, $10^{-4}$–$10^{-5}$ M in metal carbonyl compounds, were degassed by several freeze–pump–thaw cycles and examined under an argon atmosphere. Each experiment was performed with more than a tenfold excess of organic halide. The rates of atom transfer were measured by monitoring the rate of disappearance of the visible band due to $Mn(CO)_4L\cdot$.[21] Values of $\lambda_{max}$ in hexane:[8] $Mn(CO)_5\cdot$, 830 nm; $Mn(CO)_4P(n\text{-}Bu)_3\cdot$, 830 nm; $Mn(CO)_4P(O\text{-}i\text{-}Pr)_3\cdot$, 850 nm; $Mn(CO)_4P(i\text{-}Bu)_3\cdot$, 840 nm; $Mn(CO)_4P(i\text{-}Pr)_3\cdot$, 780 nm; $Mn(CO)_4PCy_3\cdot$, 740 nm. Solutions could be flashed with the xenon lamp source only once because a single flash results in substantial conversion of starting material to metal halide.

## Results and Discussion

**Reactions of Manganese Carbonyl Radicals with Organic Halides.** Photogeneration of manganese radicals, $Mn(CO)_4L\cdot$ (L = CO, $PR_3$), in the presence of organic halides, or physical mixing of persistent radical solutions, $Mn(CO)_3[PR_3]_2\cdot$, with organic halide solutions, produces the analogous metal carbonyl halide as the only reaction product other than reformed dimer (eq 6). This finding

$$Mn(CO)_{5-y}L_y\cdot + RX \rightarrow Mn(CO)_{5-y}L_yX + R \qquad (6)$$

corroborates previous observations.[19] The rate of disappearance of photogenerated radicals was evaluated by monitoring the time dependence of their visible absorption ($\lambda_{max}$ 740–840 nm[8]). Atom transfer rates involving persistent radicals were obtained by observing the decay of the intense infrared carbonyl stretch at 1855 $cm^{-1}$.[16]

All experiments were performed with at least a tenfold excess of organic halide reagent. In addition, reactions utilizing photogenerated radicals were designed so that atom transfer was at least 10 times more rapid than radical recombination. Thus the only process that needed to be taken into account in analyzing the kinetics data was the

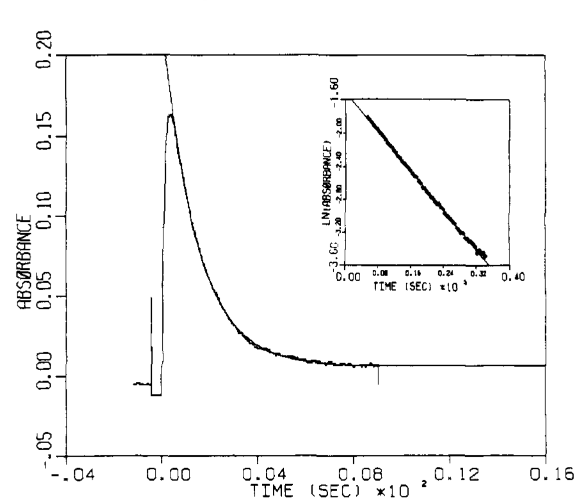

**Figure 1.** Change in absorbance vs. time at 780 nm on xenon lamp flash photolysis of a solution of $Mn_2(CO)_8[P(i\text{-}Pr)_3]_2$ ($10^{-4}$ M) and $CCl_4$ (0.208 M) in hexane under an argon atmosphere. The line through the trace represents the first-order least-squares fit of the data for disappearance of the transient. Insert: linear least-squares fit of the data to a first-order rate law expression. Every tenth data point out to 3.5 half-lives was employed. A correlation coefficient of 0.998 was determined.

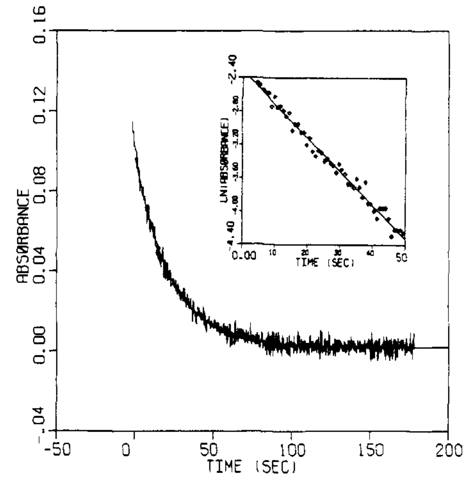

**Figure 2.** Change in absorbance vs. time at 1855 $cm^{-1}$ after hexane solutions of $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ (~ $10^{-4}$ M) and $C_6H_5CH_2Cl$ (0.040 M) were mixed. The line through the trace represents the first-order least-squares fit of the data to a first-order rate law expression. Insert: linear least-squares fit of the data to a first-order rate law expression. Every tenth data point out to 2.6 half-lives was employed. A correlation coefficient of 0.993 was determined.

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(20) (a) Forbus, N. P.; Oteiza, R.; Smith, S. G.; Brown, T. L. *J. Organomet. Chem.* **1980**, *193*, C71. (b) Rudolph, S. E.; Charbonneau, L. F.; Smith, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 7083.

(21) While a solution of $CHBr_3$ and $Mn_2(CO)_8[P(i\text{-}Pr)_3]_2$ in hexane was prepared, it was observed the $Mn(CO)_4P(i\text{-}Pr)_3Br$ forms rapidly in a thermal reaction. Infrared spectra (a germanium filter removed visible and UV radiation from the sample beam) show that the tetracarbonyl bromide is the only product.

Table I. Atom Transfer Rate Constants for Various Pairs of Organic Halides and Manganese Carbonyl Radicals

| metal carbonyl radical | $\theta$,[a] deg | organic halide | [RX], M | $k_T$, $M^{-1}$ $s^{-1}$ |
|---|---|---|---|---|
| $Mn(CO)_5\cdot$ | 95 | $CBr_4$[b] | $1.02 \times 10^{-3}$ | $(1.5 \pm 0.2) \times 10^9$ |
| $Mn(CO)_5\cdot$ | | $CHBr_3$[b] | 0.92 | $(1.04 \pm 0.03) \times 10^7$ |
| $Mn(CO)_5\cdot$ | | $C_6H_5CH_2Br$[b] | 1.34 | $(4.8 \pm 0.5) \times 10^5$ |
| $Mn(CO)_5\cdot$ | | $CH_2Br_2$[b] | neat (13.8) | $(7 \pm 1) \times 10^3$ |
| $Mn(CO)_5\cdot$ | | $CCl_4$[b] | 0.174 | $(1.4 \pm 0.1) \times 10^6$ |
| $Mn(CO)_4P(n\text{-}Bu)_3\cdot$ | 132 | $CCl_4$[b] | 0.332 | $(1.8 \pm 0.2) \times 10^6$ |
| $Mn(CO)_4P(O\text{-}i\text{-}Pr)_3\cdot$ | 130 | $CCl_4$[b] | 0.415 | $(2.2 \pm 0.1) \times 10^4$ |
| $Mn(CO)_4P(i\text{-}Bu)_3$ | 143 | $CCl_4$[c] | 0.217–0.021 | $(8.9 \pm 1.0) \times 10^4$ |
| $Mn(CO)_4P(i\text{-}Pr)_3\cdot$ | 160 | $CCl_4$[c] | 0.260–0.052 | $(2.8 \pm 0.2) \times 10^4$ |
| $Mn(CO)_4P(C_6H_{11})_3\cdot$ | 170 | $CCl_4$[c] | 0.104 | $(2.0 \pm 0.4) \times 10^4$ |
| $Mn(CO)_4P(i\text{-}Pr)_3\cdot$ | | $CH_2Br_2$[c] | 2.87–0.97 | $(8.6 \pm 0.9) \times 10^2$ |
| $Mn(CO)_4P(i\text{-}Pr)_3\cdot$ | | $CHCl_3$[c] | neat (12.4) | $(1.6 \pm 0.2) \times 10^1$ |
| $Mn(CO)_4P(C_6H_{11})_3\cdot$ | | $CHCl_3$[c] | neat (12.4) | $7.3 \pm 0.7$ |
| $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ | | $CCl_4$[d] | 0.174 | $(3.0 \pm 0.6) \times 10^4$ |
| $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ | | $C_6H_5CH_2Cl$[d] | 0.01–0.1 | $(8.0 \pm 1.6) \times 10^{-1}$ |
| $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$ | | $CH_2Cl_2$[d] | 0.010 | $(4.0 \pm 0.8) \times 10^{-2}$ |
| $Mn(CO)_3[P(i\text{-}Pr)_3]_2\cdot$ | | $CCl_4$[d] | $2.5 \times 10^{-3}$, $5.0 \times 10^{-3}$ | $(1.0 \pm 0.2) \times 10^3$ |
| $Mn(CO)_3[P(n\text{-}Bu)_3]_2\cdot$ | | $C_6H_5CH_2Cl$[d] | $1.5 \times 10^{-3}$ | $(1.0 \pm 0.2) \times 10^3$ |

[a] Phosphine cone angle, from ref 22. [b] Measured by using laser flash photolysis apparatus, 21 °C. [c] Measured by using xenon lamp flash photolysis apparatus, 24 °C. [d] Measured by using stopped flow method, 24 °C.

reaction with organic halide.

In the typical atom transfer experiment the monitored absorbance due to the radical diminishes following pseudo-first-order kinetics (Figures 1 and 2). The pseudo-first-order rate constant for reaction 7 was found to vary

$$Mn(CO)_4P(i\text{-}Pr)_3\cdot + CCl_4 \rightarrow Mn(CO)_4P(i\text{-}Pr)_3Cl + CCl_3 \qquad (7)$$

linearly with the concentration of $CCl_4$ over a concentration range 0.06–0.28 M. Thus the operable rate law is rate = $k_T[Mn(CO)_4L\cdot][RX]$. Least-squares analysis demonstrates that the $y$ intercept is within error limits of the origin, suggesting there is no other reaction occurring to a significant extent. Bimolecular atom transfer rate constants were determined for several pairs of metal-centered radicals by analysis of the pseudo-first-order decay curves, assuming that the same second-order rate law is applicable to all the systems studied. These rate constants are listed in Table I.

**Effect of Metal-Bound Phosphorus Ligand.** The electronic and steric effects of the phosphorus ligand or ligands bound to the metal center are seen in the series of rate constants for chlorine atom transfer from $CCl_4$. The steric effect of the phosphorus ligand is measured in terms of the cone angle as defined by Tolman.[22] In the series of $Mn(CO)_4L\cdot$ radicals, there is a general decrease in rate constant with increasing bulk of the ligand as measured by the cone angle. Furthermore, for L = $P(i\text{-}Bu)_3$ or $P(i\text{-}Pr)_3$ there is a distinct decrease in the rate constant in the series $Mn(CO)_5\cdot > Mn(CO)_4L\cdot > Mn(CO)_3L_2\cdot$.

While these general trends suggest a marked steric inhibition for the reaction, there is evidence in the results that increased electron donation by the ligand increases the rate of atom transfer. This is apparent in the slightly higher value for $Mn(CO)_4P(n\text{-}Bu)_3\cdot$ as compared with $Mn(CO)_5$ and also in the higher rate constant for $Mn(CO)_4P(n\text{-}Bu)_3\cdot$ as compared with $Mn(CO)_4P[O\text{-}i\text{-}Pr]_3\cdot$. Although the two ligands in the latter comparison have approximately the same cone angle, the rate is higher for the more electron-donating phosphine ligand.

Table II. Carbon-Halogen Dissociation Energies

| compd | $D$(C–X), kcal $mol^{-1}$ | ref |
|---|---|---|
| $CBr_4$ | 49.7 | 23 |
| $CHBr_3$ | 55.5 | 23 |
| $CH_2Br_2$ | 59.5 | 23 |
| $C_6H_5CH_2Br$ | 50.5 | 24 |
| $CCl_4$ | 68 | 23 |
| $CHCl_3$ | 73.5 | 23 |
| $CH_2Cl_2$ | 78.5 | 23 |
| $C_6H_5CH_2Cl$ | 60.4 | 25 |

The results thus suggest that the transition state is one in which there is a significant steric interaction between the metal-centered radical and the organic halogen atom donor. The fact that a higher electron density on the metal center promotes the reaction is consistent with a transition state that is electron demanding as compared with the ground state. Although there are no thermochemical data to lend support, these results suggest also that the Mn–Cl bond dissociation energy increases as substitution increases the electron density on the metal. By the way of contrast, the rates of recombination of $Mn(CO)_4L\cdot$ radicals to form $Mn_2(CO)_8L_2$ decrease with increasing cone angle of L but show no significant dependence on the electron donor strength of L.[8]

**Effect of the Organic Halide.** Not unexpectedly, variation in the organic halide produces large variations in atom transfer rate constants for a given metal carbonyl. For example, for $Mn(CO)_5\cdot$ $k_T$ decreases from $1.5 \times 10^9$ to $7.2 \times 10^3$ $M^{-1}$ $s^{-1}$ within a series of bromides. The reactivity order is $CX_4 > CHX_3 > C_6H_5CH_2X > CH_2X_2$. The same order was observed by Laine and Ford for reactions with $CpW(CO)_3\cdot$.[18] This ordering corresponds roughly to a decrease in the C–X bond dissociation energy (Table II). The data suggest that electronic effects dominate over steric effects in determining the variations in reaction rates among the halides. However, on this basis the values for the benzyl halides are anomalously low. This suggests that C–X bond polarity effects also play a role in determining the transition-state energy. A highly polar $C^{\delta+}$–$X^{\delta-}$ bond results in a higher activation energy because charge must be shifted off the halogen to the carbon center as the halogen atom is transferred.

Limitations on the range of rate constants that can be measured for any given radical with a halogen donor prevented us from making many direct comparisons of atom transfer rates for bromides with those for the cor-

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(22) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(23) Papulov, Y. G.; Chulkova, L. V.; Levin, V. P.; Stepanyan, A. E. *J. Struct. Chem. (Engl. Transl.)* 1972, *13*, 895. Szwarc, M. *Chem. Rev.* **1950**, *47*, 75.

(24) Lossing, F. P.; Ingold, K. U.; Henderson, I. H. S. *J. Chem. Phys.* **1954**, *22*, 1489.

(25) Benson, S. W.; DeMore, W. B. *Annu. Rev. Phys. Chem.* **1965**, *16*, 397. Evans, F. W.; Fox, R. J.; Szwarc, M. *J. Am. Chem. Soc.* **1961**, *83*, 6414.

responding chlorides. However, it seems evident from the data of Table I that the bromine transfer rates are substantially higher for a given metal carbonyl radical. This is, of course, consistent with the generally lower C–Br bond energies as compared with those for C–Cl and with the lower polarity of the C–Br bond. It is noteworthy that the rate constant for reaction of $Mn(CO)_5\cdot$ with $CBr_4$ approaches the diffusion-controlled limit. Presumably the process is overall substantially exothermic. The present results provide the first direct and extensive quantitative evaluations of halogen atom transfer rates. They substantiate that under appropriate conditions halogen atom transfer can compete with alternative reaction pathways for the radicals, such as recombination or substitution.[13]

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**Registry No.** $Mn(CO)_4P(n\text{-}Bu)_3\cdot$, 45264-38-8; $Mn(CO)_4p(o\text{-}i\text{-}Pr)_3\cdot$, 93041-25-9; $Mn(CO)_4P(i\text{-}Bu)_3\cdot$, 92186-52-2; $Mn(CO)_4P(i\text{-}Pr)_3\cdot$, 92186-53-3; $Mn(CO)_4P(C_6H_{11})_3\cdot$, 47560-29-2; $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$, 81971-50-8; $Mn(CO)_3[P(i\text{-}Pr)_3]_2\cdot$, 83634-20-2; $Mn(CO)_3[P(n\text{-}Bu)_3]_2\cdot$, 67551-64-8; $Mn(CO)_5\cdot$, 15651-51-1; $CBr_4$, 558-13-4; $CHBr_3$, 75-25-2; $C_6H_5CH_2Br$, 28807-97-8; $CH_2Br_2$, 74-95-3; $CHCl_3$, 67-66-3; $C_6H_5CH_2Cl$, 25168-05-2; $CH_2Cl_2$, 75-09-2; $CCl_4$, 56-23-5; $Cl_2$, 7782-50-5; $Br_2$, 7726-95-6.

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# Formation and Chemistry of the Homologous Series of Nitrido Clusters: $[Ru_4N(CO)_{12}]^-$, $[Ru_5N(CO)_{14}]^-$, and $[Ru_6N(CO)_{16}]^-$ †

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The reaction of coordinated isocyanate ligands to give new nitrido clusters is explored. The thermolysis of $[Ru_4(NCO)(CO)_{13}]^-$ gives $[Ru_4N(CO)_{12}]^-$ in 78% recrystallized yield after 24 h. When the trinuclear isocyanate clusters $[Ru_3(NCO)(CO)_{10}]^-$ and $[Ru_3(NCO)(CO)_{11}]^-$ are heated with 1 equiv of $Ru_3(CO)_{12}$, the hexanuclear nitrido cluster $[Ru_6N(CO)_{16}]^-$ can be isolated in 82% yield. $[Ru_6N(CO)_{16}]^-$ reacts rapidly with CO at room temperature to give $[Ru_5N(CO)_{14}]^-$ in quantitative yield. A single-crystal X-ray crystallographic study of $(PhCH_2Et_3N)[Ru_5N(CO)_{14}]$ [$P\bar{1}$ space group, $a = 12.123$ (6) Å, $b = 14.263$ (5) Å, $c = 10.642$ (3) Å, $\alpha = 104.74$ (3)°, $\beta = 93.28$ (3)°, $\gamma = 80.25$ (4)°, $Z = 2$] revealed a square-based pyramid of metal atoms with the nitrogen positioned slightly below the square face. Other interconversions among the nitrido clusters are also discussed. At high CO pressure, the isocyanate ligand can be reformed from the nitrido clusters.

## Introduction

The source of nitrogen in almost all the known nitrido clusters is one form or another of nitric oxide. Practically, nitrosonium ion and preformed metal nitrosyl complexes are used to form nitrido clusters.[3] The only cluster that does not make use of NO is $[Ru_6N(CO)_{16}]^-$, as reported in the preliminary communication of this work.[4] In this case, isocyanate is the species donating the nitrogen atom. One of the reasons we are interested in these nitrido clusters is to establish a relationship with the structures and reactivity of surface-coordinated nitrogen atoms. These latter species are invoked as intermediates in many important catalytic reactions such as the Haber process[5] and the reduction of $NO_x$ pollutants.[6]

One of the interesting features of metals that catalyze eq 1 is the appearance of isocyanates on the metal surface

$$2NO + CO \rightarrow N_2O + CO_2 \qquad (1)$$

during the catalytic reaction.[7] It has been suggested that the isocyanate arises by eq 2, which must obviously be

$$N(ads) + CO(ads) \rightleftharpoons NCO(ads) \qquad (2)$$

reversible for the catalyst to be active. Other workers[8] have capitalized on this reaction as a means of forming a new N–C bond by adding $H_2$ to the mixture of NO and CO. The end result (eq 3) is the catalytic synthesis of isocyanic acid.

$$NO + 2CO + {}^1/{}_2H_2 \rightarrow HNCO + CO_2 \qquad (3)$$

As mentioned above this paper discusses the conversion of $NCO^-$ coordinated to clusters into nitrido clusters. Besides generating three new nitrido clusters, the reactions bear a similarity to the surface chemistry.

## Experimental Section

PPN(Cl)[9] (PPN = bis(triphenylphosphine)nitrogen(1+)), $PPN(N_3)$,[10] PPN(NCO),[10] $Ru_3(CO)_{12}$,[11] $PPN[Ru_4(NCO)(CO)_{13}]$,[12] $(PPN)_2[Ru_6(CO)_{18}]$,[13] and $PPN[Ru(CO)_3(NO)]$[14] were prepared according to published procedures. Tetrahydrofuran (THF) and

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(1) NSF Predoctoral Fellow, 1982–1985.

(2) Alfred P. Sloan Fellow, 1983–1985.

(3) Gladfelter, W. L. *Adv. Organomet. Chem.*, in press.

(4) Blohm, M. L.; Fjare, D. E.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1004–1006.

(5) Osaki, A.; Aika, K. *Catal. Sci. Technol.* **1981**, *1*, 87.

(6) Eisenberg, R.; Hendriksen, D. E. *Adv. Catal.* **1979**, *28*, 79–172.

(7) Unland, M. L. *J. Phys. Chem.* **1973**, *77*, 1952–1956.

(8) Voorhoeve, R. J. H.; Trimble, L. E. *J. Catal.* **1978**, *54*, 269–280.

(9) Ruff, J. K.; Schlentz, W. J. *Inorg. Synth.* **1974**, *15*, 85–87.

(10) Martinsen, A.; Songstad, J. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 645–650.

(11) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1976**, *16*, 47–48.

(12) Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1774–1780.

(13) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980**, *383*–392.

(14) Stevens, R. E.; Fjare, D. E.; Blohm, M. L.; Gladfelter, W. L., Paper 153, 17th Great Lakes Regional Meeting of the American Chemical Society, St. Paul, MN, June 1983; American Chemical Society: Washington, DC, 1983.

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