Contribution from the School of Chemical Sciences,
University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

Steric and Electronic Effects on Atom Transfer Reactions of Re(CO)₄L· Radicals with Organic Halides and HSn(n-C₄H₉)₃[1]

John M. Hanckel, Kang-Wook Lee, Paul Rushman, and Theodore L. Brown*

Received April 10, 1985

Re(CO)₄L· (L = CO, P(OR)₃, PR₃, AsEt₃) radicals, generated by laser flash photolysis of L(CO)₄Re–Re(CO)₄L, react with halogen atom donors (CH₂Br₂, CHCl₃, CCl₄) or hydrogen atom donors (HSn(n-Bu)₃) in solution to produce *cis*-Re(CO)₄LX (X = H, Cl, Br). Bimolecular rate constants for halogen and hydrogen atom transfers to Re(CO)₄L· were measured by following the decay of the transient Re(CO)₄L· absorbance in the 550-nm region. The rate constants for both the halogen and hydrogen atom transfer processes are influenced by steric and electronic properties of the substituent L. Both bromine and chlorine atom transfer processes depend to a similar extent on the electronic properties of L. The bromine atom transfer reactions show a slightly greater steric dependence than the chlorine atom transfer reactions. The steric dependence of the hydrogen atom transfer reaction is similar to that of the halogen atom transfers, but the dependence on the electronic properties of L is smaller. Increasing electron density at the metal center enhances the rate of atom transfer; polar effects are more evident in the halogen atom transfer. Rate constants for both atom transfer reactions fit a two-parameter free energy relationship, wherein electronic and steric effects of L are represented.

Introduction

Metal-centered radicals of transition-metal carbonyls have been the subjects of extensive study.[2] Although persistent 17e metal carbonyl radicals are known,[3] numerous transient metal carbonyl radicals can be produced by irradiation into the $\sigma \rightarrow \sigma^*$ or $d_\pi \rightarrow \sigma^*$ transition of dinuclear carbonyl compounds[4] (eq 1). Such photogenerated metal-centered radicals recombine rapidly (eq 2);[5] they have also been shown to undergo electron-transfer (eq 3),[2g] ligand substitution (eq 4),[2h,4d,6] and atom abstraction (eq 5)[2g–i,3b,5d,7] reactions.

$$[M(CO)_xL_y]_2 \xrightarrow{h\nu} 2M(CO)_xL_y \cdot \qquad (1)$$

$$2M(CO)_xL_y \cdot \rightarrow [M(CO)_xL_y]_2 \qquad (2)$$

$$M(CO)_xL_y \cdot + A \rightarrow M(CO)_xL_y^+ + A^- \cdot \qquad (3)$$

$$M(CO)_xL_y \cdot + L' \rightarrow M(CO)_{x-1}L_yL' \cdot + CO \qquad (4)$$

$$M(CO)_xL_y \cdot + X{-}Y \rightarrow M(CO)_xL_yX + Y\cdot \qquad (5)$$

Knowledge of the electronic absorption spectrum of the photogenerated radical provides a means for following its reactions; bimolecular rate constants for recombination and halogen atom abstraction processes have been determined for Mn(CO)₄L·[5f,8] and Re(CO)₅·[7] by such direct observation. Reaction of Mn(CO)₄L· (L = CO, P(O-i-Pr)₃, P(n-Bu)₃, P(i-Bu)₃, P(C₆H₁₁)₃) with halogen donors such as CCl₄, CH₂Br₂, PhCH₂Br, or CHCl₃ produces *cis*-Mn(CO)₄LX in each case.[8]

Significant steric and electronic influences of the substituent L on atom transfer rates were evident, although there has not been a systematic study of these effects.

To probe the steric, electronic, and solvent effects on atom transfer rates, we report herein the results of a kinetic study of an extensive series of halogen and hydrogen atom abstraction reactions of Re(CO)₄L· (L = CO, PR₃, P(OR)₃, AsEt₃) radicals, generated by nitrogen laser (337 nm) flash photolysis. Reaction rates were determined by observing the decay of the Re(CO)₄L· absorption band in the 550-nm range.

Experimental Section

Materials. Re₂(CO)₁₀ was obtained from Pressure Chemical Co. and used without further purification. Phosphines and AsEt₃ were purchased from Strem Chemical Co. and used in the preparation of Re₂(CO)₈L₂ complexes without additional purification. Tributyltin hydride, HSn(n-Bu)₃, was obtained from Sigma Chemical Co. or Alfa Products and used as received. Halogenated hydrocarbons were obtained from standard vendors. Carbon tetrachloride was washed with hot alcoholic KOH three times, washed with H₂O/CaCl₂, and then distilled from P₂O₅. Methylene bromide and chloroform were washed with H₂SO₄, H₂O, dilute NaOH, and H₂O/CaCl₂ and then distilled from P₂O₅. Hexane was treated with H₂SO₄, washed with H₂O and aqueous NaHCO₃, and then distilled from CaH₂. Acetonitrile was distilled twice from P₂O₅. Toluene and pyridine were distilled from CaH₂. THF was distilled from sodium–sodium benzophenone ketyl. All distillations were carried out under N₂ or Ar. All distilled reagents and solvents were freeze–pump–thaw degassed three times and stored in an N₂ atmosphere drybox.

Re₂(CO)₈L₂ (L = P(i-Bu)₃, P(n-Bu)₃, P(i-Pr)₃, PCy₃, PMe₃, P-(OMe)₃, P(O-i-Pr)₃, AsEt₃) were prepared by the method of Nubel and Brown[9] and purified by chromatography on a silica gel column eluted with 5:1 hexane/CH₂Cl₂. Re₂(CO)₈L₂, where L = P(i-Bu)₃, P(n-Bu)₃, P(i-Pr)₃, PCy₃, P(OMe)₃, has 1,2-diaxial geometry as judged by the pattern of CO stretching modes in the IR region. Each of the others (L = PMe₃, P(O-i-Pr)₃, AsEt₃) was assigned 1,2-diequatorial geometry based on a comparison of IR spectra with the known compounds Re₂-(CO)₈(PMe₃)₂ and Re₂(CO)₈[P(OPh)₃]₂.[9]

Kinetics Technique. The laser flash photolysis apparatus has been described previously.[8]

Samples for flash photolysis were prepared in a drybox and loaded into a 25-mL round-bottom flask that was connected to a 1 cm path length

(1) This research was supported by the National Science Foundation through Research Grant CHE 83-12331.
(2) (a) Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80. (b) Howard, J. A.; Morton, J. R.; Preston, K. F. *Chem. Phys. Lett.* **1981**, *83*, 226. (c) Fairhurst, S. A.; Morton, J. R.; Preston, K. F. *J. Chem. Phys.* **1982**, *77*, 5872. (d) Lionel, T.; Morton, J. R.; Preston, K. F. *J. Phys. Chem.* **1982**, *86*, 367. (e) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (f) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (g) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258. (h) Fox, A.; Malito, J.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (i) Laine, R. M.; Ford, P. C. *Inorg. Chem.* **1977**, *16*, 388. (j) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.
(3) (a) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496. (b) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, *2*, 775.
(4) (a) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 4246. (b) Hughey, J. L., IV; Bock, C. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440. (c) Freeman, A.; Bersohn, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 4116. (d) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.
(5) (a) Hughey, J. L., IV; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49. (b) Wegman, R. W.; Olsen, R. J.; Gard, D. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089. (c) Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 3748. (d) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249. (e) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536. (f) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259.
(6) (a) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095. (b) McCellen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007. (c) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700.
(7) Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 1842.
(8) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42.
(9) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644.
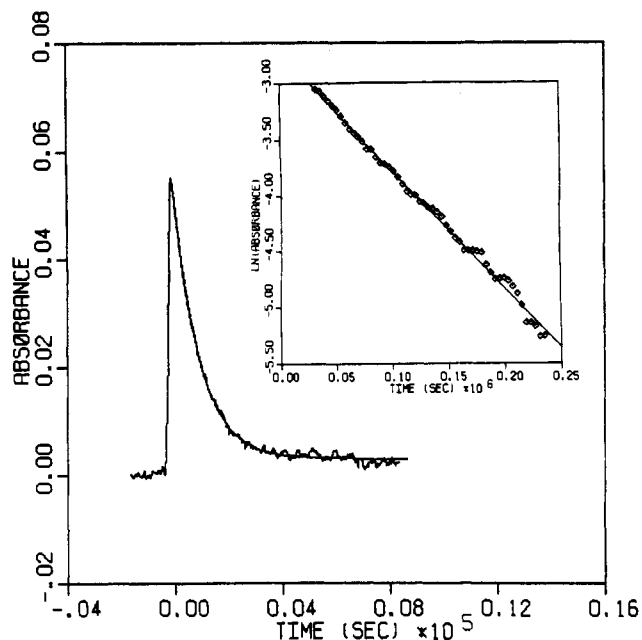
Figure 1. Change in absorbance vs. time at 550 nm upon laser flash photolysis of $Re_2(CO)_8(PMe_3)_2$ (10^{-4} M) and $CHCl_3$ (0.50 M) in hexane under nitrogen. The line through the trace represents the first-order least-squares fit of the data for disappearance of the transient. The insert gives a linear-least-square fit of the data to a first-order rate expression. Data for more than 3 half-lives were employed.

Figure 2. Variation in k_{obsd} with CCl_4 concentration in the reaction of $Re(CO)_4P(i-Pr)_3$· with CCl_4.

Figure 3. Variation in k_{obsd} with $HSn(n-Bu)_3$ concentration in the reaction of $Re(CO)_4PMe_3$· with $HSn(n-Bu)_3$.

quartz cuvette by glass tubing. The entire sample container was sealed with a threaded Teflon stopcock. The solutions were typically 2.0×10^{-4} to 4.0×10^{-4} M in dinuclear carbonyl and at least 20 times more concentrted in halocarbon or $HSn(n-Bu)_3$. Halocarbon or $HSn(n-Bu)_3$ concentrations were sufficiently high so that decay of the $Re(CO)_4L$· transient absorbance was at least 10 times faster than decay observed for recombination of $Re(CO)_4L$· radicals. All reactions were carried out at ambient temperature (22 ± 2 °C).

The approximate position of λ_{max} for each $Re(CO)_4L$· radical was located by measurement of the change in optical density vs. λ (450–650 nm) upon flash photolysis of the $Re_2(CO)_8L_2$ compounds: $Re(CO)_5$·, 550 (±10) nm; $Re(CO)_4PMe_3$·, 560 (±10) nm; $Re(CO)_4P(n-Bu)_3$·, 560 (±10) nm; $Re(CO)_4P(i-Pr)_3$·, 560 (±10) nm; $Re(CO)_4AsEt_3$·, 540 (±10) nm; $Re(CO)_4P(O-i-Pr)_3$·, 550 (±10) nm. The observed λ_{max} for $Re(C-O)_5$· of 550 nm is in reasonable agreement with the value of 535 nm found for $Re(CO)_5$· in ethanol by Meckstroth et al.[7] (The k_{obsd} values calculated from transient decays were not significantly altered when based upon data taken 20 nm on either side of λ_{max}.)

Results

Flash Photolysis of $Re_2(CO)_8L_2$. Laser flash photolysis (337 nm) of hexane solutions of $Re_2(CO)_8L_2$ produces transient absorption spectra in the 550-nm region. Decays of transients within 500 µs follow second-order kinetics and are unaffected by the presence of CO in solution. Absorption maxima are thus assigned to $Re(CO)_4L$· radicals.

The flash-photogenerated $Re(CO)_4L$· radicals either react with halogen atom or hydrogen atom donors to produce cis-$Re(CO)_4LX$ (X = halogen, hydrogen) or recombine to form the dinuclear parent, as indicated by the IR spectra of samples subjected to flash photolysis. Although in reactions of $HSn(n-Bu)_3$ with $Mn(C-O)_3L_2$· small amounts of $Mn(CO)_3L_2Sn(n-Bu)_3$ were formed,[3a] there was no evidence for a $Re(CO)_4LSn(n-Bu)_3$ species in IR spectra of solutions subjected to flash photolysis. Neither was there evidence of such secondary reaction in the kinetics of reactions between $Re(CO)_4L$· and $HSn(n-Bu)_3$.

Each experiment was designed so that recombination of the carbonyl radicals made an insignificant contribution to the transient decay; further, the amount of halogen or hydrogen atom donor was in all cases sufficient to make the atom transfer reaction pseudo first order over several half-lives, as exemplified by the results shown in Figure 1.

A plot of k_{obsd} values for the reaction of $Re(CO)_4P(i-Pr)_3$· and CCl_4 vs. the CCl_4 concentration is linear, with zero y intercept
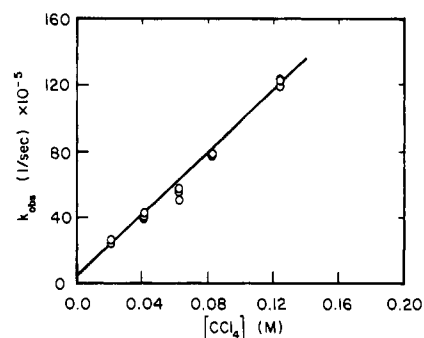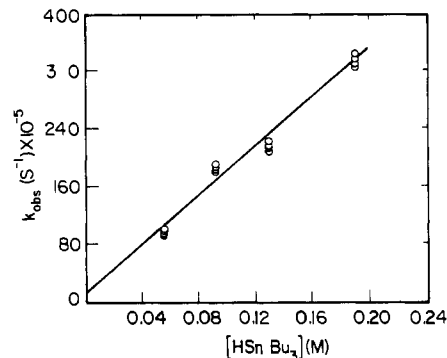
within the error limits, as shown in Figure 2 (linear-least-squares error limits calculated at the 95% confidence level). Thus, the reaction of $Re(CO)_4P(i-Pr)_3$· and CCl_4 is first order in CCl_4. The bimolecular rate constant k_T, calculated from the slope of the line in Figure 2, has the value 9.3×10^7 M^{-1} s^{-1}. The reactions of other $Re(CO)_4L$· radicals with halogen donors were assumed to follow the same rate law; the corresponding rate constants are listed in Table I. In cases where the k_T value is close to the diffusion-controlled rate constant ($k_{diff} = 1.1 \times 10^{10}$ M^{-1} s^{-1}),[10] the activation rate constants (k_{act}) are estimated from the equation $1/k_T = 1/k_{act} + 1/k_{diff}$.[11] Where appropriate, k_{act} values are also given in Table I.

The rate law for the reaction between $Re(CO)_4PMe_3$· and $HSn(n-Bu)_3$ was established in a similar manner, by reaction of $Re(CO)_4PMe_3$· with several different concentrations of $HSn(n-Bu)_3$ under pseudo-first-order conditions (Figure 3). The slope of the line in Figure 3 yields a rate constant, k_T, of 1.7×10^8 M^{-1} s^{-1}. Again, other $Re(CO)_4L$· radicals were assumed to react with $HSnBu_3$ by the same law; the corresponding rate constants are listed in Table II.

Reactions of $Re(CO)_4L$· in hexane solution were in general faster than the corresponding reactions in acetonitrile solution. Rate constants for the reaction of $Re(CO)_4(PMe_3)$· with CH_2Br_2 in several different solvents are shown in Table I. Variations in k_T as a function of solvent are small; the largest value of k_T is found in hexane solution (1.8×10^9 M^{-1} s^{-1}) and the smallest in THF solution (5.1×10^8 M^{-1} s^{-1}). The results do not yield a reasonable correlation between k_T and solvent dielectric constant, or solvent donor ability (donor number (DN) or $\Delta\nu_{MeO-D}$[12]). These small solvent effects may indicate that the transition state entails only minimal charge separation.

(10) k_{diff} in cyclohexane at 22 ± 2 °C is estimated to be 3.7×10^9 M^{-1} s^{-1}.[2j] Since k_{diff} is inversely linear with viscosity, k_{diff} in hexane can be estimated by using hexane and cyclohexane viscosities ($10^3\eta = 8.98$ and 2.92, respectively).

(11) (a) Noyes, R. M. *Prog. React. Kinet.* **1961**, *1*, 129. (b) Marcus, R. A.; Siders, P. *J. Phys. Chem.* **1982**, *86*, 622.

(12) For definitions and values of these solvent parameters, see: Dack, M. J. R. In *Techniques of Chemistry*; Weissberger, A., Ed.; Wiley: New York, 1976; Vol. VIII.

Table I. Halogen Atom Transfer Rate Constants for Reactions of Various Organic Halides and Re(CO)₄L·

L	$\delta_{CO}{}^a$	θ, deg^b	solvent	CH₂Br₂		CHCl₃		CCl₄	
				[CH₂Br₂], M	$10^{-7}k_T$, M^{-1} s^{-1}	[CHCl₃], M	$10^{-5}k_T$, M^{-1} s^{-1}	[CCl₄], M	$10^{-7}k_T$, M^{-1} s^{-1}
CO	0.00	95	hexane	0.10	4.8 ± 0.2	0.95	4.4 ± 0.1	0.10	4.9 ± 0.2
PMe₃	5.05	118	hexane	0.005	180 ± 10 (210)^d	0.50	210 ± 10	0.002	250 ± 10 (320)^d
P(OMe)₃	3.18	107	hexane	0.028	15 ± 1	1.0	15 ± 1	0.005	33 ± 1
P(O-i-Pr)₃	3.90	130	hexane	0.14	8.1 ± 0.2	0.50	9.3 ± 0.1	0.010	20 ± 1
P(n-Bu)₃	5.69	132	hexane	0.086	39 ± 3	0.50	54 ± 1	0.010	76 ± 3
P(i-Bu)₃	5.40	143	hexane	0.36	2.7 ± 0.2	0.50	4.5 ± 0.3	0.050	8 ± 0.5
P(i-Pr)₃	6.20	160	hexane	0.58	1.4 ± 0.2	0.50	4.0 ± 0.3	0.02 – 0.12	9.3 ± 0.6
PCy₃	6.32	170	hexane	0.30	1.5 ± 0.1	0.50	3.0 ± 0.3	0.050	7.4 ± 0.6
AsEt₃	5.33	128^c	hexane	0.057	74 ± 8 (79)	0.50	87 ± 1	0.005	130 ± 10 (150)
CO	0.00	95	CH₃CN	0.21	5.1 ± 0.3				
PMe₃	5.05	118	CH₃CN	0.014	87 ± 6 (96)				
			toluene	0.007	85 ± 4 (99)				
			THF	0.007	51 ± 1				
			pyridine	0.014	61 ± 3				
P(OMe)₃	3.18	107	CH₃CN	0.071	8.9 ± 0.3				
P(O-i-Pr)₃	3.90	130	CH₃CN	0.14	3.4 ± 0.2				
P(n-Bu)₃	5.69	132	CH₃CN	0.043	22 ± 2				
P(i-Bu)₃	5.40	143	CH₃CN	0.28	1.6 ± 0.1				
P(i-Pr)₃	6.20	160	CH₃CN	0.071	0.85 ± 0.13				
AsEt₃	5.33	128^c	CH₃CN	0.043	37 ± 2				

$^a\delta_{CO}$ is the ^{13}C chemical shift for Ni(CO)₃L, reported downfield from Ni(CO)₄. All chemical shift data were taken from ref 21. ^{b}Phosphine cone angle from ref 14. ^{c}Approximation, see text. ^{d}The values in parentheses are the rate constants corrected for diffusion effects (see text).

Table II. Hydrogen Atom Transfer Rate Constants for the Reaction of HSn(n-Bu)₃ with Re(CO)₄L·

L	$\delta_{CO}{}^a$	θ, deg^b	[HSn(n-Bu)₃], M	$10^{-7}k_T$, M^{-1} s^{-1}
CO	0.00	95	0.19	5.1 ± 1.1
PMe₃	5.05	118	0.056–0.19	17 ± 1
P(n-Bu)	5.69	132	0.19	5.1 ± 0.6
P(O-i-Pr)₃	3.90	130	0.19	1.5 ± 0.1
P(i-Bu)₃	5.40	143	0.38	0.53 ± 0.3
P(i-Pr)₃	6.20	160	0.30	0.13 ± 0.02
AsEt₃	5.33	128^c	0.93	7.3 ± 0.05
P(OMe)₃	3.18	107	0.074	6.4 ± 0.3
PCy₃	6.32	170	0.089	0.41 ± 0.02

^{a}Reference 21. ^{b}Phosphine cone angle from ref 14. ^{c}Approximation, see text.

Discussion

Reaction of Re(CO)₄L· with CCl₄, CHCl₃, and CH₂Br₂. The rate constant for reaction of Mn(CO)₄L· (L = P(n-Bu)₃, P(i-Pr)₃, P(i-Bu)₃, P(C₆H₁₁)₃) with CCl₄ diminishes as the cone angle of L increases.[8] A similar effect is observed in reactions of Re(CO)₄L· with RX: L = PMe₃ > P(n-Bu)₃ > P(i-Bu)₃ > P(i-Pr)₃ ≈ PCy₃. It has been suggested that the 5-coordinate, 17-electron carbonyl radicals have a square-pyramidal geometry.[2b,3,13] Ligands such as phosphine that replace CO are thought to take up one of the basal positions. In M(CO)₃L₂· radicals the two ligands may occupy trans-basal positions.[3] If Re(CO)₄L· radicals are also square-pyramidal with L in the basal plane, then the origin of the steric effect is clear. The geometry of the observed products, cis-Re(CO)₄LX, is in accord with the suggested geometry of the radicals.

The relationship between the cone angle[14] of L and ln k_T for the reaction of Re(CO)₄L· with CH₂Br₂ is shown in Figure 4. The cone angle of AsEt₃ has not been measured, but it can be estimated to be about 128°, slightly smaller than its phosphine analogue (PEt₃ cone angle 132°).[14,15] With the exception of L = P(i-Bu)₃, points corresponding to substituents with similar electronic
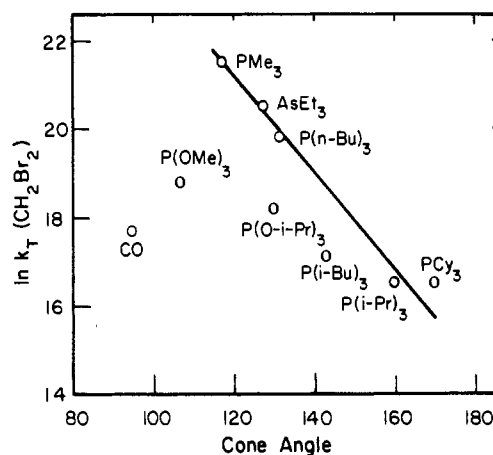
Figure 4. Dependence of ln k_T for bromine atom transfer from CH₂Br₂ to Re(CO)₄L· on the cone angle (θ) of L.

characteristics (L = PMe₃, P(n-Bu)₃, AsEt₃, P(i-Bu)₃, P(i-Pr)₃, PCy₃) are approximately collinear.

The electronic characteristics of substituent L are also manifested in the data. Large negative deviations from the relationship in Figure 4 for the points corresponding to L = CO and P(OMe)₃ indicate that Re(CO)₅· and Re(CO)₄(P(OMe)₃)· react more slowly than would be predicted on the basis of their cone angles. The deviation from linearity for L = P(O-i-Pr)₃, while smaller, is also probably traceable to its greater π-acceptor ability as compared with that of the other ligands in the series. This trend parallels that found for the reaction of Mn(CO)₄L· (L = CO, P(O-i-Pr)₃, P(n-Bu)₃) with CCl₄; it is consistent with the suggestion that the transition state in such reactions is electron-demanding.[8]

Since both electronic and steric properties of the substituent L are expressed in the rate constants, it is reasonable to suppose that the data should fit a two-parameter free energy relationship, as in eq 6.[14,16–18] The steric parameter, θ, is readily defined in

$$\ln k = a\delta + b\theta + c \tag{6}$$

(13) (a) Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7515. (b) Huber, H.; Kundig, E. P.; Ozin, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 5585.
(14) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(15) Jackson, R. A.; Poë, A. *Inorg. Chem.* **1978**, *17*, 997.

(16) (a) Heimback, P.; Kluth, J.; Schenkluhn, H.; Weimann, B. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 569–571. (b) Schenkluhn, H.; Berger, R.; Pittel, B.; Zahres, M. *Transition Met. Chem. (Weinheim, Ger.)* **1981**, *6*, 277–287.

Table III. Coefficients for the Free Energy Relationship $\ln k_T = a\delta + b\theta + c$

| atom donor	solvent	a	b	c	correln coeff
CH₂Br₂	hexane	1.4	−0.14	31	0.925
CH₂Br₂	CH₃CN	1.2	−0.14	30	0.929
CHCl₃	hexane	1.3	−0.12	24	0.921
CCl₄	hexane	1.3	−0.11	29	0.935
HSn(n-Bu)₃	hexane	0.87	−0.13	30	0.973
CCl₄/Mn(CO)₄L·[a]	hexane	0.82	−0.13	25	0.821

[a] Data from ref 8 were used to calculate the a and b values.
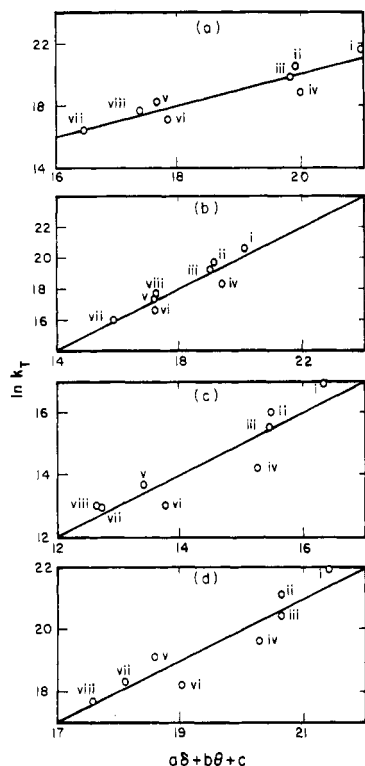
Figure 5. Plots of $\ln k_T$ vs. $a\delta + b\theta + c$ for each series of halogen-transfer reactions showing the scatter of points about the line of identity: (a) RX = CH₂Br₂, solvent hexane; (b) RX = CH₂Br₂, solvent acetonitrile; (c) RX = CHCl₃, solvent hexane; (d) RX = CCl₄, solvent hexane. The ligands are PMe₃ (i), AsEt₃ (ii), P(n-Bu)₃ (iii), P(OMe)₃ (iv), P(O-i-Pr)₃ (v), P(i-Bu)₃ (vi), P(i-Pr)₃ (vii), and CO (viii).

terms of the cone angle.[14] The electronic parameter, δ, might be associated with ligand pK_a,[2f,18-20] but this would preclude use of data where L = CO and AsEt₃. Further, to the extent that π-back-bonding contributions are important in influencing the availability of electron density at the metal center, pK_a values do not provide an accurate measure of electronic characteristics across the range of ligands studied here. Bodner has reported ¹³C NMR chemical shift values for an extensive list of Ni(CO)₃L complexes.[21] Good linear correlations between the carbonyl chemical shift data (δ_{CO}) and the A₁ ν(CO) frequencies in Ni(CO)₃L were found. Additional linear correlations between δ_{CO} for Ni(CO)₃L complexes and δ_{CO} for several other metal carbonyl complexes containing L were noted. Thus, Bodner has suggested that the
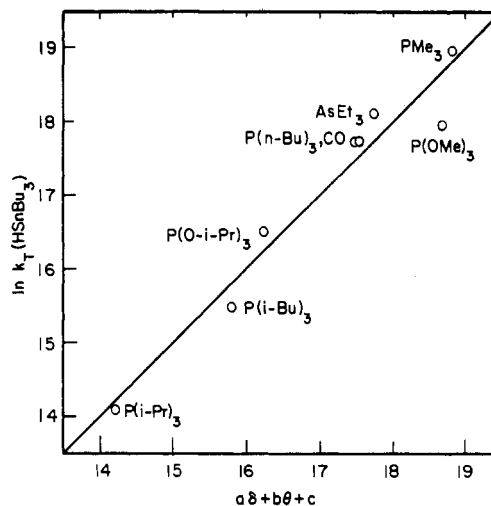
Figure 6. Correlation between $\ln k_T$ for the hydrogen atom transfer from HSn(n-Bu)₃ to Re(CO)₄L· in hexane and the combined steric and electronic effects of various ligands.

chemical shift data could be used as an electronic effect parameter.[21,22]

With use of δ_{CO} data for the Ni(CO)₃L complexes as the electronic parameter in eq 6, the values of coefficients a and b obtained for the reaction of Re(CO)₄L· radicals with RX are listed in Table III. The multiple linear regression analysis yields a correlation coefficient of greater than 0.92 between experimental and calculated values of $\ln k_T$ (Figure 5).

Reaction of Re(CO)₄L· with HSn(n-Bu)₃. HSn(n-Bu)₃ is regarded as an excellent hydrogen atom donor.[23] The persistent metal-centered radicals Mn(CO)₃L₂·[3a] and Re(CO)₃[P(C₆H₁₁)₃]₂·[3b] have been shown to undergo hydrogen atom transfer reactions with HSn(n-Bu)₃ to give HM(CO)₃L₂ compounds. On the other hand, other metal carbonyl radicals, e.g., Co(CO)₃PR₃· and CpMo(CO)₃· appear to react with HSn(n-Bu)₃ via an oxidative addition of the Sn–H bond to the metal center, accompanied by CO loss, to produce ultimately Co(CO)₃PR₃Sn(n-Bu)₃ or CpMo(CO)₃Sn(n-Bu)₃ and H₂.[24,25]

Each of the Re(CO)₄L· radicals listed in Table II reacts with HSn(n-Bu)₃ to produce *cis*-HRe(CO)₄L. As with the halogen atom abstraction reactions, there is a significant rate dependence on the bulk of L. Application of multivariate analysis to these data in terms of the two-parameter model of eq 6 yields the correlation shown in Figure 6. Values of a and b are 0.87 and −0.13, respectively (Table III).

Comparison of Halogen and Hydrogen Atom Abstraction Processes. The plots in Figure 5 reveal a remarkably consistent pattern of scatter of points about the line of identity from one series of halogen atom transfer reactions to another. The points for L = P(OMe)₃ and P(i-Bu)₃ fall consistently below the line, whereas those for L = AsEt₃, P(O-Pr)₃, and PMe₃ fall consistently a bit above the line. This suggests that one or another of the parameters for each of these ligands is in error. It seems likely that the steric parameter is inappropriate, at least in the cases of P(i-Bu)₃ and P(OMe)₃. In the former case, the β branching in the alkyl group probably results in blockage of access to the metal center that is inadequately reflected in the cone angle. Similarly, the lone pairs on oxygen in the phosphite may lead to a larger effective steric requirement. The literature values[14] for the cone angles

(17) (a) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (b) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61–73.

(18) Golovin, M. N.; Rahman, M. M.; Belmonte, J. E.; Giering, W. P. *Organometallics* **1985**, *4*, 1981.

(19) Shi, Q.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 71.

(20) Rerek, M. E.; Basolo, F. *Organometallics* **1983**, *2*, 372.

(21) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

(22) We have chosen to represent ligand effects in terms of a two-parameter model, in analogy with the approach followed previously by others.[14,16,17] Our results do not suggest the need to include additional parameters that separately account for differential π-donor or π-acid behavior of the ligands.[18] In short, a single electronic parameter that reflects the ligand contribution to the integrated density at the metal center seems sufficient.

(23) Narayanan, B. A.; Kochi, J. K. *J. Organomet. Chem.* **1984**, *272*, C49 and references therein.

(24) Wegman, R. W.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 2494.

(25) Wegman, R. W.; Brown, T. L. *Organometallics* **1982**, *1*, 47.

for P(*i*-Bu)₃ (143°) and P(OMe)₃ (107°) appear to systematically underestimate their sizes. The values of (150 ± 2)° and (115 ± 2)°, respectively, place the points for these two ligands on the line in Figure 5. Additional work is in progress to more clearly define the role of ligand steric properties in radical reactions.

Inspection of Table III shows that the electronic parameters for the halogen atom transfer reactions are all quite similar. The corresponding value of *a* for chlorine atom transfer to Mn(CO)₄L· radicals, 0.82, is considerably smaller than for the Re radicals. A smaller value for *a* indicates a lower sensitivity of the reaction to varitions in electron density at the metal. The value of *a* for hydrogen atom transfer to the Re radicals is also smaller than for the halogen atom transfer reactions. This is the expected result; the transition state for hydrogen atom transfer should be less electron-demanding of the metal than for halogen atom transfer.

The steric parameter for halogen atom transfer to Re(CO)₄L· radicals is larger for bromine than for chlorine, as expected. The comparatively large value of *b* for hydrogen atom transfer may reflect the small covalent radius of hydrogen, which requires close

approach in the atom transfer step.

The kinetics data for the atom transfer processes studied here do not in themselves reveal the degree of electron-transfer character in the rate-determining process. Both halogen and hydrogen atom transfers are quite fast, even though the transition states in the two cases should differ markedly in polarity. There is evidence in the comparative values for *a* that the transition state for halogen atom transfer is more electron-demanding, but more work is needed to establish whether there is a regular relationship between the rate constant for halogen atom transfer and electron-acceptor ability of the halogen atom donor.

Registry No. Re(CO)₅, 15684-00-1; Re(CO)₄P(OMe)₃, 101697-74-9; Re(CO)₄P(*i*-Pr)₃, 101697-75-0; Re(CO)₄AsEt₃, 101697-73-8; Re-(CO)₄PMe₃, 101697-76-1; Re(CO)₄P(*n*-Bu)₃, 101697-77-2; Re(CO)₄P-(*i*-Bu)₃, 101697-78-3; Re(CO)₄PCy₃, 101697-79-4; CH₂Br₂, 74-95-3; CHCl₃, 67-66-3; CCl₄, 56-23-5; HSn(*n*-Bu)₃, 688-73-3; Br₂, 7726-95-6; Cl₂, 7782-50-5; H₂, 1333-74-0.

Contribution from the Department of Chemistry,
Arizona State University, Tempe, Arizona 85287

The "Inert-Pair Effect" on Electronegativity

R. T. Sanderson[†]

The quantitative theory of polar covalence has been used to calculate the electronegativity of major group metals in oxidation states lower than their maximum, from experimental bond energies. Presumably by reducing the effective nuclear charge, lone-pair electrons significantly reduce the electronegativity. For example, the value on the relative compactness scale for thallium(I) is only 0.99 compared to 2.25 for thallium (III); for lead(II) it is 1.92 compared to 2.29 for lead(IV). This causes bond polarity to be higher than otherwise expected in compounds exhibiting the lower oxidation states, which in turn accounts for increased stability and other commonly observed differences in physical and chemical properties. Bond energies calculated by using the new electronegativities agree with the experimental values within an average of less than 2% for 55 gaseous compounds of major group elements in lower oxidation states.

The "inert-pair effect" long familiar to inorganic chemists is a term to designate the phenomenon in which certain of the heavier major group metals exhibit a valence less by 2 than expected from their electronic configuration and corresponding periodic grouping. In a general way it has been explained by Pitzer[1] and by Pykko and Descalux[2] as a relativistic effect causing the outer s electrons to be more strongly attracted to the nucleus than normally expected. For many years it has been suspected that the compounds resulting from the inert-pair effect have more polar bonds than might be expected from merely a reduction in valence.[3] However, in a recent revision of electronegativities of the major group elements[4] based on the relative compactness of the electronic clouds of their atoms, values for lower oxidation states were omitted because of lack of quantitative knowledge of the inert-pair effect. The purpose of this paper is to describe an attempt to evaluate these additional electronegativities, using the quantitative theory of polar covalence as a basis for back-calculating the electronegativity values from experimental heats of formation and atomization energies.

Method of Calculation

According to the quantitative theory of polar covalence,[5] a polar covalent bond derives its energy from two contributions, one covalent and the other ionic. The covalent contribution is simply a portion of the maximum possible covalent energy, E_c, which is the geometric mean of the two homonuclear bond energies, E_{AA} and E_{BB}, corrected for any difference between the actual bond length, R_0, and the nonpolar covalent radius sum, R_c ($= r_A + r_B$), by the factor, R_c/R_0:

$$E_c = R_c(E_{AA}E_{BB})^{1/2}/R_0$$

Table I. Effects of Inert-Pair and Single Electrons on Electronegativities of M2, M3, and M4 Elements in Various Oxidation States[a]

element	oxidn state (from a number of examples)			
	I	II	III	IV
Be	1.56 (3)	**1.81**		
Ca	1.13 (2)	**0.95**		
B	1.53 (3)	2.19 (2)	**2.28**	
Al	0.84 (4)	1.63 (2)	**1.71**	
Ga	0.86 (4)		**2.42**	
In	0.71 (3)		**2.14**	
Tl	0.99 (3)		**2.25**	
Si	2.08 (2)		1.99 (2)	**2.14**
Ge		0.56 (4)		**2.62**
Sn		1.49 (3)		**2.30**
Pb		1.92 (4)		**2.29**

[a] Boldface numerals are electronegativities for the usual oxidation states.

The maximum ionic energy, E_i, is assumed to be the Coulombic attraction between unit opposite charges separated by the bond length:

$$E_i = 33200/R_0$$

The factor 33 200 converts the energy to kilocalories per mole and must of course be multiplied by the factor 4.184 to be converted to kilojoules per mole, both assuming distance to be measured in picometers. The two energies are apportioned according to the partial charges. The ionic blending coefficient, t_i, is half the difference between the two partial

(1) Pitzer, K. S. *Acc. Chem. Res.* **1979**, *12*, 271–276.
(2) Pykko, P.; Desclaux, J.-P. *Acc. Chem. Res.* **1979**, *12*, 276–281.
(3) Sanderson, R. T. *Inorganic Chemistry*; Reinhold: New York, 1967.
(4) Sanderson, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 2259–2261.
(5) Sanderson, R. T. *Polar Covalence*; Academic: New York, 1983.

[†] Present address: 4725 Player Drive, Fort Collins, CO 80525.