Ligand Effects on Organometallic Substitution Reactions

Jim D. Atwood,* Michael J. Wovkulich, and David C. Sonnenberger

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

Received July 12, 1982 (Revised Manuscript Received February 23, 1983)

One of the simplest methods for modifying the chemical reactivity of an atom is to alter the groups bound to that atom. For organic reactions the changing reactivity is attributed to substituent effects, while the term for transition-metal reactions is ligand effects.[1-5] In organometallic substitution reactions a ligand may change the mechanism through variable bonding capabilities as shown by methyl and nitrosyl complexes[6-12] or may modify the rate of reaction without modifying the mechanism.[13-18] It is the latter type of reactivity on which this Account centers. The ligand environment may affect the rate of reactions at a metal center by stabilizing the transition state or by destabilizing the ground state.

The majority of the data pertaining to ligand effects on organometallic reactions have been obtained on 18 electron complexes that undergo rate-determining loss of a two-electron ligand leading to a 16-electron transition state. The transition state for ligand dissociation corresponds to almost complete rupture of the M–L bond.[13,14] Several experiments have shown that the energy difference between the transition state and the coordinatively unsaturated intermediate is small and that there is very little discrimination in reactions of the intermediate with nucleophiles.[19-23]

Our primary premise is that electron-donating ligands on the metal stabilize the electron-deficient transition state formed in a dissociative process, thus accelerating the rate of the reaction. While this concept has seldom been applied to inorganic systems, the ability of electron-donating groups to stabilize the transition state of S_N1 reactions for X replacement of RX is well-known in organic chemistry. A similar, though opposite, explanation is accepted for the trans effect in associative reactions of square-planar complexes, where the ability of the trans ligand to accept excess electron density provided by the attacking nucleophile stabilizes the transition state. Thus there is considerable precedence for the importance of bonding capability in the transition state. With some consideration of ligand effects in the ground state, the ability of ligands to provide

Table I
Rate Constants for Dissociation of L from $Cr(CO)_4L_2$ and $Cr(CO)_5L$ at 130 °C

L	10^6k, s^{-1}		$k(bis)/$
	bis	mono	$k(mono)^b$
$P(OMe)_3$	9.22	0.548	8.4
$P(OPh)_3$	397	15.7	12.7
PPh_3	3.9×10^6	99.7	4×10^4
PBu_3	1380	0.0065^a	2×10^5
$AsPh_3$	very fast	11600	
CO	130	130	1

^{a} Calculated from the equilibrium constant and the rate constant for the reverse reaction. ^{b} Corrected for the statistical factor of two ligands for the bissubstituted complex.

electron density to the transition state allows an understanding of the effect of ligand environment on dissociative reactions of mononuclear, dinuclear, and polynuclear organometallic complexes.

Mononuclear Complexes

An investigation of CO exchange reactions in octahedral metal carbonyls showed a cis labilization of CO dissociation and an extensive cis-labilization order was developed from the large body of CO dissociation reactions.[13-16] This labilization was accounted for in terms of a "site preference model", a stabilization of the transition state by the presence of the ligand in the radial position of a square-pyramidal transition state.[15,16] To obtain more information on ligand effects on ground-state and transition-state energies, we have

Jim D. Atwood obtained a B.S. from Southwest Missouri State University in 1971. His Ph.D. work at the University of Illinois under the direction of T. L. Brown resulted in the Theron Standish Piper Award for Graduate Research in Inorganic Chmeistry in 1975. This was followed by Postgraduate Study in the Joint U.S.–U.S.S.R. Program of Cooperation in Homogeneous Catalysis sponsored by the National Science Foundation and The Soviet Academy of Sciences with E. L. Muetterties at Cornell University and A. E. Shilov at the Institute of Chemical Physics. He joined the faculty of the State University of New York at Buffalo in 1977, pursuing his interest in mechanistic organometallic chemistry and achieving his current rank of Associate Professor. Jim Atwood is an Alfred P. Sloan Research Fellow, 1983–1985.

Michael J. Wovkulich received his B.S. from the State University College at Cortland, New York, in 1976, an M.A. in 1979, and his Ph.D. in 1981 from the State University of New York at Buffalo. He is currently doing postdoctoral research with J. W. Suggs at Brown University.

David C. Sonnenberger received his B.S. at Canisius College in 1977 and his Ph.D. from the State University of New York at Buffalo in 1981. During his graduate studies he held both Woodburn and Graduate School Fellowships. He is currently engaged in postdoctoral research with T. J. Marks at Northwestern University.

(1) See for example Basolo, F.; Pearson, R. "Mechanisms of Inorganic Reactions"; Wiley: New York, 1967.
(2) Ballhausen, C. J. "Introduction to Ligand Field Theory"; McGraw Hill: New York, 1962.
(3) Basolo, F.; Pearson, R. G. *Prog. Inorg. Chem.* 1964, 4, 381.
(4) Basolo, F.; Chatt, J.; Gray, H. B.; Pearson, R. G.; Shaw, B. L. *J. Chem. Soc.* 1961, 2207.
(5) Tobe, M. L. "Inorganic Reaction Mechanisms"; Nelson: London, 1972.
(6) Angelici, R. J. *Organomet. Chem. Rev.* 1968, 3, 173.
(7) Dobson, G. R. *Acc. Chem. Res.* 1976, 9, 300.
(8) Darensbourg, D. J. *Adv. Organomet. Chem.* 1982, 21, 113.
(9) Cawse, J. W.; Fiato, R. A.; Pruett, R. L. *J. Organomet. Chem.* 1979, 172, 405.
(10) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* 1977, 99, 2527.
(11) Thorsteinson, E. M.; Basolo, F. *J. Am. Chem. Soc.* 1966, 88, 3929.
(12) Wawersik, H.; Basolo, F. *J. Am. Chem. Soc.* 1967, 89, 4626.
(13) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* 1975, 97, 3380.
(14) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* 1976, 98, 3155.
(15) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* 1976, 98, 3160.
(16) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* 1978, 100, 366.
(17) Wovkulich, M. J.; Atwood, J. D. *J. Organomet. Chem.* 1980, 184, 77.
(18) Wovkulich, M. J.; Feinberg, S. J.; Atwood, J. D. *Inorg. Chem.* 1980, 19, 2608.
(19) Covey, W. D.; Brown, T. L. *Inorg. Chem.* 1973, 12, 2820.
(20) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* 1973, 12, 1286.
(21) Day, J. P.; Basolo, F.; Pearson, R. G. *J. Am. Chem. Soc.* 1968, 90, 6927.
(22) Cardaci, G.; Narciso, V. *J. Chem. Soc., Chem. Commun.* 1972, 2298.
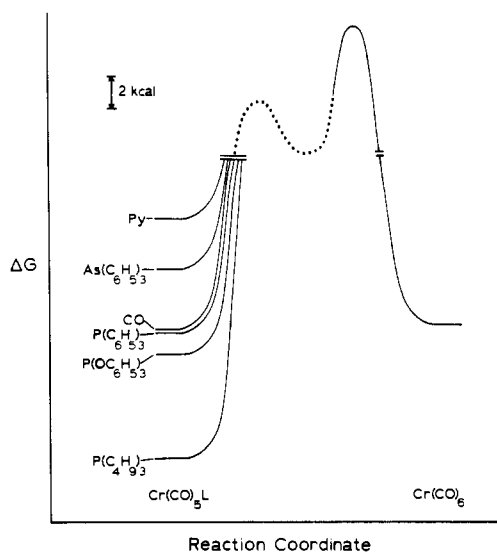(23) Kelley, J. M.; Herman, H.; VonGustorf, E. K. *J. Chem. Soc., Chem. Commun.* 1973, 105.

Figure 1. The relative ground-state energies of $Cr(CO)_5L$ species, evaluated by the principle of microscopic reversibility, vary over a wide range, which is indicated and semiquantitatively.

investigated a series of chromium carbonyl complexes.[17,18,24] Reaction of $Cr(CO)_5L$ with CO to yield $Cr(CO)_6$ (eq 1) proceeds with rate-determining dissociation

$$Cr(CO)_5L + CO \rightleftarrows Cr(CO)_6 + L \qquad (1)$$

of L.[17] Since the activation parameters are known for the reaction in both directions, one may calculate the relative ground-state energies of the $Cr(CO)_5L$ complexes to provide a measure of the Cr–L bond strength.[17] The bond energies, as shown in Figure 1, are in the order $Cr–PBu_3 > Cr–P(OMe)_3 > Cr–P(OPh)_3 > Cr–PPh_3 \sim Cr–CO > Cr–AsPh_3 >> Cr–NR_3$ and vary over a range of 15 kcal/mol. This trend is similar in order and magnitude to that observed previously in platinum chemistry and may be used as the relative ground-state energies for organometallic complexes.[25] The reactions of the bissubstituted complexes, *trans*-$Cr(CO)_4L_2$, show that the trans ligand is important in determining rates of dissociation (eq 2). Table I shows

$$Cr(CO)_4L_2 + CO \rightarrow Cr(CO)_5L + L \qquad (2)$$

a comparison of the mono- and bissubstituted complexes. In each case ligand dissociation from the bissubstituted complex occurs more rapidly than from the corresponding monosubstituted complex. For trans phosphites the acceleration is by a factor of 10, while for trans phosphines the rate acceleration is by factors of 10^4–10^5, suggesting that the trans ligand is important.[18] To further examine the effect of the trans ligand, we prepared and investigated the reactivity of the series of complexes, *trans*-$Cr(CO)_4LL'$[24] (eq 3). These

$$\textit{trans-}Cr(CO)_4LL' + CO \rightarrow Cr(CO)_5L + L' \qquad (3)$$
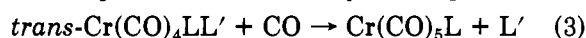
reactions were quite selective in proceeding to a single product; the rate constants are given in Table II.[24] The ligand that dissociates from $Cr(CO)_4LL'$ is the weaker binding ligand ($AsPh_3$, PPh_3, or $P(OPh)_3$) as revealed by the kinetics data for $Cr(CO)_5L$ compounds (Figure 1). The order of L' bond strength, for any given L in the trans position is, $Cr–PBu_3 > Cr–P(OMe)_3 > Cr–P(OPh)_3 > Cr–PPh_3 > Cr–AsPh_3$. If the transition state

(24) Wovkulich, M. J.; Atwood, J. D. *Organometallics* **1982**, *1*, 1316.
(25) Manzer, L. E.; Tolman, C. A. *J. Am. Chem. Soc.* **1976**, *97*, 1955.

Table II
First-Order Rate Constants for Dissociation of L'
from *trans*-$Cr(CO)_4LL'$

L	L'	temp, °C	k, s⁻¹
PPh₃	PPh₃	50	$(1.96 \pm 0.02) \times 10^{-4}$
		55	$(4.29 \pm 0.02) \times 10^{-4}$
		60	$(8.73 \pm 0.08) \times 10^{-4}$
P(OPh)₃	PPh₃ ᵃ	80	$(3.61 \pm 0.13) \times 10^{-5}$
		90	$(1.63 \pm 0.01) \times 10^{-4}$
		100	$(6.23 \pm 0.06) \times 10^{-4}$
P(OPh)₃	AsPh₃	60	$(1.24 \pm 0.36) \times 10^{-4}$
		65	$(2.45 \pm 0.12) \times 10^{-4}$
		70	$(4.70 \pm 0.17) \times 10^{-4}$
P(OMe)₃	PPh₃	100	$(2.10 \pm 0.11) \times 10^{-4}$
		105	$(3.88 \pm 0.14) \times 10^{-4}$
		110	$(7.58 \pm 0.13) \times 10^{-4}$
P(OMe)₃	P(OPh)₃	110	$(1.44 \pm 0.07) \times 10^{-5}$
		120	$(5.41 \pm 0.08) \times 10^{-5}$
		130	$(1.81 \pm 0.02) \times 10^{-4}$
PBu₃	PPh₃	70	$(1.72 \pm 0.02) \times 10^{-4}$
		75	$(3.43 \pm 0.05) \times 10^{-4}$
		80	$(6.79 \pm 0.11) \times 10^{-4}$
PBu₃	AsPh₃	35	$(1.79 \pm 0.02) \times 10^{-4}$
		40	$(3.67 \pm 0.03) \times 10^{-4}$
		45	$(7.19 \pm 0.11) \times 10^{-4}$
PBu₃	P(OPh)₃	115	$(2.73 \pm 0.11) \times 10^{-4}$
		120	$(4.83 \pm 0.16) \times 10^{-4}$
		125	$(8.50 \pm 0.34) \times 10^{-4}$
PBu₃	P(OMe)₃	110	$(1.18 \pm 0.03) \times 10^{-5}$
		120	$(4.29 \pm 0.07) \times 10^{-5}$
		130	$(1.60 \pm 0.03) \times 10^{-4}$

ᵃ Both $P(OPh)_3$ and PPh_3 dissociate at equal rates.

Table III
Activation Enthalpies (kcal/mol) for Dissociation
of L' from $Cr(CO)_4LL'$

L	L'			
	P(OMe)₃	P(OPh)₃	PPh₃	AsPh₃
PPh₃		36.6 ± 1.3	31.3 ± 1.2	
PBu₃	39.2 ± 1.6	34.6 ± 0.4	32.4 ± 0.5	26.5 ± 0.5
P(OPh)₃		37.6 ± 1.0	36.6 ± 1.3	29.7 ± 0.3
P(OMe)₃	43.4 ± 0.6	38.1 ± 0.1	35.7 ± 1.6	

Table IV
Leaving-Group Effects for the Reaction
$Cr(CO)_4LL' + CO \rightarrow Cr(CO)_5L + L'$ at 130 °Cᵃ

L	L'		
	P(OPh)₃	PPh₃	AsPh₃
PPh₃	2.7 × 10⁻²	3.9	
PBu₃	1.46 × 10⁻³	2.3 × 10⁻¹	6.3
P(OPh)₃	4.0 × 10⁻⁴	2.7 × 10⁻²	3.6 × 10⁻¹
P(OMe)₃	1.8 × 10⁻⁴	8.1 × 10⁻³	
CO	1.6 × 10⁻⁵	1.0 × 10⁻⁴	1.0 × 10⁻²

ᵃ The numbers are first-order rate constants quoted as reciprocal seconds.

represents complete removal of L' as suggested,[17-24] then the transition state for any given L ($Cr(CO)_4L$) would be the same and the activation parameters should be a measure of the ground-state energies as shown in Figure 1.[24] Table III shows the activation enthalpies. The differences in energy for constant L are similar for each L and similar to the values for $Cr(CO)_5L$ and for the platinum complexes previously studied.[17,25] This correlation of activation parameters with the thermodynamic parameters lends support to the idea of complete dissociation of L' in the transition state.[17-24]

For a given dissociating ligand, the rate varies with the nature of the trans ligand, a trans effect.[24] The rate

Table V
Relative Rates for PPh_3 Dissociation from
trans-$Cr(CO)_4LPPh_3$ at 130 °C
and the $Cr-PPh_3$ Bond Lengths

L	rel rate	$Cr-PPh_3$ bond distance, Å
PBu_3	2400	2.345 (3)[b]
$P(OPh)_3$	130	2.393 (1)[b]
$P(OMe)_3$	81	2.362 (2)[b]
CO	1	2.422 (1)[c]

[a] Since the activation enthalpies are different for each ligand the choice of temperature can affect the ratio of rate constants.   [b] Reference 26.   [c] Reference 32.
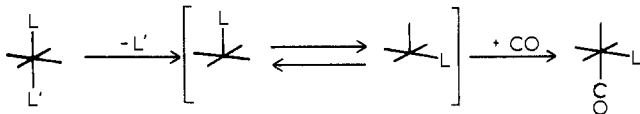
Table VI
Bond Lengths and Infrared Stretching Frequencies
for Substituted Metal Carbonyl Complexes

compd	M–C(trans)	M–C(cis)	ref	ν(asym stretch),[c] cm^{-1}
$Cr(CO)_6$	1.909 (7)	1.909 (7)	a	1985
$Cr(CO)_5P(OPh)_3$	1.861 (4)	1.861 (4)	b	1960
$Cr(CO)_5PPh_3$	1.845 (4)	1.880 (4)	c	1945

[a] Whitaker, A.; Jeffrey, J. W. *Acta Crystallogr.* 1967, *23*, 977.   [b] Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* 1974, *12*, 265.   [c] Wovkulich, M. J.; Atwood, J. D. *J. Organomet. Chem.* 1980, *184*, 77.

Figure 2. The reaction scheme suggested for dissociation of L′ from $Cr(CO)_4LL'$, showing the rearrangement of the five-coordinate intermediate.

constants are shown in Table IV. The rate of PPh_3 dissociation from *trans*-$Cr(CO)_4L(PPh_3)$ varies by more than 10^4 as L changes through the series PPh_3 > PBu_3 > $P(OPh)_3$ > $P(OMe)_3$ > CO. Because the trans ligands in an octahedral complex share both σ and π bonding orbitals, one would anticipate that the trans ligand would affect the energetics for loss of the ligand trans to it. To examine possible ground-state contributions to the reactivity, we have determined (in collaboration with Professor J. L. Atwood) the structures of the complexes (*trans*-$Cr(CO)_4L(PPh_3)$ (L = PBu_3, $P(OMe)_3$, and $P(OPh)_3$).[26] The $Cr-PPh_3$ bond lengths and rate constants for dissociation of PPh_3 are shown in Table V. While the $Cr-PPh_3$ bond lengths vary significantly through the series, the bond lengths do not correlate with the rates of PPh_3 dissociation. Indeed the complex with the longest $Cr-PPh_3$ bond length (L = CO) is the slowest to dissociate PPh_3. Clearly ground-state properties are not the primary factor in this kinetic trans effect for octahedral carbonyl complexes.[24,30] The trans effect order is similar to the order seen for cis labilization, which also was explained by transition-state stabilization.[15,24] The important difference is the location of the stabilizing ligand in the transition state. For cis labilization the ligand stabilizing the transition state occupies a basal site in the square pyramid.[11,12] In the operation of the trans effect in $Cr(CO)_4LL'$, the ligand occupies an axial site in the transition state.[24] The reaction scheme is shown in Figure 2. Calculations have shown that the basal location of a ligand would be more stable than the axial, and this rearrangement

(26) Atwood, J. L.; Wovkulich, M. J.; Atwood, J. D., manuscript in preparation.
(27) In this explanation the reason for stereospecific CO dissociation is that the trans CO would be bound more strongly to the metal because of ligand effects in the ground state. We are not suggesting that ligand site preference does not exist; calculations have shown that the ligand favors a basal position.[16] We are suggesting that a σ-donating ligand in the basal or apical position will stabilize the transition state.
(28) The order of the trans effect correlates with steric size, but we have been unable to find any evidence for steric interactions in these reactions. One cannot rule out the possibility of rearrangement of the octahedron to the cis complex prior to dissociation,[29] but there is no evidence for rearrangement in the complexes.[24]
(29) Darensbourg, D. J.; Kudarosoki, R.; Schenk, W. *Inorg. Chem.* 1982, *21*, 2488.
(30) The bond lengths are within the range normally observed for Cr-phosphine and Cr-phosphite bonds.[31-33]

is shown in the scheme.[16] Thus the highest energy point (the transition state) for L′ loss from $Cr(CO)_4LL'$ must involve the presence of L in the apical position of the square-pyramidal species, and there must exist a stabilization of that transition state depending on the nature of L. The similarity of the cis-labilization and trans-effect orders in octahedral complexes suggests that a stabilization of the transition state does not depend on the specific site occupied by the ligand in the transition state; a stabilization that depends on the nature of L exists and is in the same order whether the ligand occupies an axial or a basal site in the transition state.[15,16,24,27,28]

The source of the stabilization of the unsaturated, 16-electron transition state is related to the σ-donor strength.[24] A stronger σ donor creates more electron density at the metal and stabilizes the unsaturated transition state. This simple explanation allows an understanding of cis labilization and of the trans effect observed for $Cr(CO)_4LL'$. In cis labilization, the presence of the ligand would stabilize the transition state, accounting for the labilization, but the labilization would exist whether dissociation occurs cis or trans to the labilizing ligand. Dissociation occurs cis to the labilizing ligand because of ground-state effects. A strong σ donor or a weak π acceptor strengthens the trans M–CO bond. This is shown by bond distances and infrared stretching frequencies in Table VI. Thus the cis ligand labilizes through transition-state stabilization and directs the dissociation to the cis position by strengthening the trans M–CO bond. The order of the trans effect for dissociation from $Cr(CO)_4LL'$ does not represent a direct correlation with the σ-donor ability on the ligands, although the gross features do correlate with phosphines having a larger effect than phosphites, which in turn are more labilizing than CO.[19]

To completely understand the order observed, we must consider not only the stabilization of the transition state but the effect of the trans ligand on the bonding in the ground state. The best information on ground-state effects comes from the structures of $Cr(CO)_4$-(PPh_3)L. For L = PBu_3 the $Cr-PPh_3$ bond length is short (2.345 (3) Å), an indication of strengthening of the $Cr-PPh_3$ bond by the presence of PBu_3 in the trans position.[26] This ground-state strengthening partially offsets the transition-state stabilization expected for $Cr(CO)_4PBu_3$. The result is that $Cr(CO)_4(PPh_3)_2$ dissociates PPh_3 more rapidly than $Cr(CO)_4(PBu_3)PPh_3$. Similarly the $Cr-PPh_3$ bond length is much shorter for L = $P(OMe)_3$ than for L = $P(OPh)_3$, leading to the near equivalence in rates though $P(OMe)_3$ is a stronger σ donor than $P(OPh)_3$. Thus the trans-effect order is

controlled by the ability of a ligand to place electron density on the metal in the transition state, but the fine points require consideration of the ground-state effects also. This intermingling of ground-state effects and transition-state effects is shown in the reaction of Cr-$(CO)_4(P(OPh)_3)PPh_3$.[24] As discussed earlier $P(OPh)_3$ is bound more strongly than PPh_3 to organometallic centers and the ground state for $P(OPh)_3$ loss would be lower than that for PPh_3 loss by 2–4 kcal/mol. Since the rates are almost the same for loss of PPh_3 and $P(OPh)_3$ from $Cr(CO)_4(PPh_3)(P(OPh)_3)$, the transition state represented by $Cr(CO)_4PPh_3$ must be lower in energy than the transition state represented by Cr-$(CO)_4P(OPh)_3$ by an amount that is almost equal to the ground-state energy difference between a $Cr–P(OPh)_3$ and $Cr–PPh_3$ bond (2–4 kcal/mol).

In cases where the ground-state and transition-state effects cooperate, large rate enhancements may be anticipated. Examples are the trans-$Cr(CO)_4L_2$ complexes where L = phosphine. As shown in Table I the rate of dissociation of L is 10^5 more rapid than that from the monosubstituted complexes. For these complexes the transition state, $Cr(CO)_4L$, would be more stable than for L dissociation from $Cr(CO)_5L$, and the bonding (ground state) would also be weakened by the buildup of electron density along the axis; thus the large rate enhancement for phosphine dissociation. The observation of dissociation of $P(OMe)_3$ from cis-$Mo(CO)_4$-$(P(OMe)_3)PCy_3$, while consistent with steric acceleration, also leads to a transition state ($Mo(CO)_4PCy_3$) in which molybdenum would have more electron density than if PCy_3 dissociated.[34]

The gross ligand effects observed in mononuclear complexes can be completely explained by considering that the electron-deficient transition state is stabilized by a ligand that can donate electron density to the metal, although the fine features require a consideration of ground-state effects.

Dinuclear Compounds

Substitution reactions of $Mn_2(CO)_9L$ with further ligand lead to the disubstituted product, ligated at both manganese centers.[35] The rate of the second substitution (eq 4), which proceeds by CO dissociation, de-

$$Mn_2(CO)_9L + L \rightarrow Mn_2(CO)_8L_2 + CO \qquad (4)$$

pends on the nature of the ligand:[35]

	L = PPh_3	> PBu_3	> $P(OPh)_3$	> CO
rel rate	44	12	1.5	1

The rate acceleration and order are similar to those observed for mononuclear complexes as discussed earlier. Substitution on $Re_2(CO)_{10}$ proceeds directly to $Re_2(CO)_8L_2$, suggesting that a similar rate acceleration exists for $Re_2(CO)_9L$.[36] Substitution on $Co_2(CO)_8$ also leads to disubstituted product.[37,38] For most ligands

(31) Holladay, A.; Churchill, M. R.; Wong, A.; Atwood, J. D. *Inorg. Chem.* 1980, *19*, 2195.

(32) Plastas, H. J.; Stewart, J. M.; Grim, S. O. *Inorg. Chem.* 1973, *12*, 265.

(33) Preston, H. S.; Stewart, J. M.; Plastas, H. J.; Grim, S. O. *Inorg. Chem.* 1972, *11*, 161.

(34) Darensbourg, D. J.; Graves, A. H. *Inorg. Chem.* 1979, *18*, 1257.

(35) Wawersik, H.; Basolo, F. *Inorg. Chim. Acta* 1969, *3*, 113.

(36) Haines, L. I. B.; Poë, A. J. *J. Chem. Soc. A* 1969, 2826.

(37) Absi-Halabi, M.; Atwood, J. D.; Forbes, N. P.; Brown, T. L. *J. Am. Chem. Soc.* 1980, *102*, 6248.

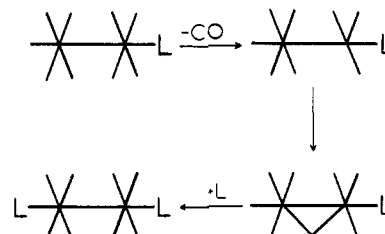(38) Forbes, N. P.; Brown, T. L. *Inorg. Chem.* 1981, *20*, 4343.

Figure 3. Suggested scheme for the labilization of CO dissociation from $Mn_2(CO)_9L$ in comparison to $Mn_2(CO)_{10}$. The transition state for loss of CO from $Ir_4(CO)_{10}L_2$.

Table VII
Estimated Rates of Substitution of $MnRe(CO)_{10}$
Derivatives at 150 °C

$MnRe(CO)_{10}$[a]	1.3×10^{-3} s^{-1}
$PPh_3(CO)_4MnRe(CO)_5$[b]	3.7×10^{-3} s^{-1}
$(CO)_5MnRe(CO)_4PPh_3$[b]	7×10^{-4} s^{-1}

[a] Fawcett, J. P.; Poë, A. *J. Chem. Soc., Dalton Trans.* 1976, 2039. [b] Fawcett, J. P.; Poë, A. J.; Twigg, M. V. *J. Organomet. Chem.* 1973, *61*, 315.

this reaction proceeds by a different mechanism, but for $AsPh_3$ and $P(t$-Bu$)_3$ the substitution occurs by a CO dissociative route. The appearance of the disubstituted product indicates that a similar acceleration may exist in dinuclear cobalt complexes.[37,38] In contrast, substitution on $MnRe(CO)_{10}$ leads to the monosubstituted product, $MnRe(CO)_9L$, and then to disubstituted product at a slightly slower rate.[28]

The similarity of the labilization of CO dissociation in $Mn_2(CO)_9L$ to that in mononuclear complexes indicates a common origin of the rate effects, but in the dinuclear compound the substitution occurs at the unsubstituted center.[35] We have suggested that substitution on $Mn_2(CO)_9L$ proceeds by the series of reactions shown in Figure 3.[15,39] The ligand accelerates CO dissociation at the substituted manganese center by relieving the electronic unsaturation in the coordinatively unsaturated transition state. For steric reasons further substitution cannot occur at the manganese. A CO from the unsubstituted manganese moves to a bridging position to share the unsaturation between the two manganese centers and the incoming ligand substitutes at the previously unsubstituted manganese.[39]

Since the ligand accelerates CO dissociation at the substituted site, the observed similarity to the rate enhancements in mononuclear complexes is expected. We have suggested a mechanism similar to that in Figure 3 to explain substitutions on $MnRe(CO)_{10}$ that lead to the rhenium-substituted product, even though CO dissociation from manganese should occur 100 times more rapidly than from rhenium.[39] The observation that CO dissociation is not enhanced for $MnRe(CO)_9L$ over that in $MnRe(CO)_{10}$ is a natural consequence of these considerations. The ligand on rhenium would accelerate CO dissociation by less than a factor of 100; the precise enhancement would depend on the nature of the ligand.[40] Thus CO would be expected to dissociate from the unsubstituted manganese or the substituted rhenium at comparable rates with no real ac-

(39) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* 1980, *102*, 3484.

(40) The formation of the bissubstituted product cannot be determined quantitatively because of overlap of the infrared bands. Qualitatively $MnRe(CO)_8(PPh_3)_2$ and $MnRe(CO)_8(PBu_3)_2$ were formed at the same rate and more rapidly than $MnRe(CO)_8(P(OPh_3)_3)_2$.[41]

Table VIII
Relative Rates of CO Dissociation from
Transition-Metal Carbonyl Clusters

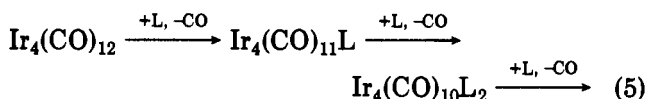| n	$Ru_3(CO)_{12-n}$-$(PPh_3)_n$[a]	$Co_4(CO)_{12-n}$-$(P(OMe)_3)_n$[b]	$Ir_4(CO)_{12-n}$-$(PPh_3)_n$[c]
0	1	1	1
1	55	0.9	220
2	40	1.3	3500

[a] Reference 42.   [b] References 43–45.   [c] Reference 46.

celeration for $(CO)_5MnRe(CO)_4L$ over $MnRe(CO)_{10}$.

The rates of substitution on the manganese- and rhenium-substituted isomers of $MnRe(CO)_9PPh_3$ have been estimated and are shown in Table VII. Substitution of PPh_3 on manganese causes an acceleration of CO dissociation relative to $MnRe(CO)_{10}$, while substitution of PPh_3 on rhenium causes a slight slowing of further substitution, consistent with our suggested mechanistic scheme (Figure 3). The observation of slightly slower CO dissociation from the rhenium-substituted isomer of $MnRe(CO)_9L$ than from $MnRe(CO)_{10}$ is not inconsistent with ligand stabilization of the transition state and indeed provides further confirmation of the mechanistic scheme.

Transition-Metal Clusters

The presence of donor ligands on metal clusters also leads to more rapid CO dissociation, as shown in Table VIII. Use of PPh_3 with $Ru_3(CO)_{12}$ or $Ir_4(CO)_{12}$ has shown considerable labilization for further substitution,[42,46] but use of $P(OMe)_3$ with $Co_4(CO)_{12}$ gave essentially no change in rate with the extent of substitution.[43-45] We have examined each step of the substitution reactions on $Ir_4(CO)_{12}$ for the ligands PBu_3, PPh_3, $P(OPh)_3$, $AsPh_3$, and CO[47-49] (eq 5). These substituion

$$Ir_4(CO)_{12} \xrightarrow{+L, -CO} Ir_4(CO)_{11}L \xrightarrow{+L, -CO}$$
$$Ir_4(CO)_{10}L_2 \xrightarrow{+L, -CO} \quad (5)$$

reactions proceed predominantly by CO dissociation with the rate dependent on the nature of the coordinated ligand but not the concentration of the incoming ligand.[47-49] For CO dissociation from $Ir_4(CO)_{11}L$, the dependence on L is[48]

$$
\begin{array}{cccccc}
& L = PBu_3 & > PPh_3 & > AsPh_3 & > P(OPh)_3 & > CO \\
k^{51} & 1100 & 520 & 320 & 50 & 6.0
\end{array}
$$

This order precisely parallels the σ-donor strength, suggesting that similar effects to those in mononuclear and dinuclear complexes are operative in Ir_4; a σ-donor ligand stabilizes the coordinatively unsaturated transition state. Dissociation of CO from the disubstituted clusters shows a further labilization.[49]

$$
\begin{array}{cccccc}
& L = PPh_3 & \sim AsPh_3 & > PBu_3 & > P(OPh)_3 & > CO \\
\text{rel rate} & 1200 & & 540 & 21 & 1
\end{array}
$$

(41) Sonnenberger, D.; Atwood, J. D., unpublished results.
(42) Malik, S. K.; Poë, A. *Inorg. Chem.* **1978**, *17*, 1484.
(43) Darensbourg, D. J.; Incorvia, M. J. *J. Organomet. Chem.*, **1979** *171*, 89.
(44) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1980**, *19*, 2585.
(45) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1981**, *20*, 1911.
(46) Karel, K. J.; Norton, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 6812.
(47) Sonnenberger, D.; Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 3243.
(48) Sonnenberger, D.; Atwood, J. D., *J. Am. Chem. Soc.* **1982**, *104*, 2113.
(49) Sonnenberger, D.; Atwood, J. D. *Organometallics* **1982**, *1*, 694.

Table IX
Relative Rates of CO Dissociation from the
Tetrairidium Carbonyl Clusters

cluster	rel rate[a]
$Ir_4(CO)_{12}$[b]	1
$Ir_4(CO)_{11}P(OPh)_3$[c]	8
$Ir_4(CO)_{10}(P(OPh)_3)_2$[d]	21
$Ir_4(CO)_{11}AsPh_3$[c]	54
$Ir_4(CO)_{11}PPh_3$[c]	82
$Ir_4(CO)_{11}PBu_3$[c]	170
$Ir_4(CO)_{10}(PBu_3)_2$[d]	540
$Ir_4(CO)_{10}(PPh_3)_2$[d]	1200
$Ir_4(CO)_{10}(AsPh_3)_2$[d]	1200

[a] Rate from $Ir_4(CO)_{12}$ was defined as unity.   [b] Reference 35.   [c] Reference 36.   [d] Reference 37.

The order for $Ir_4(CO)_{10}L_2$ is slightly different than that of $Ir_4(CO)_{11}L$ but is very similar to that seen for Mn_2-$(CO)_9L$ although the magnitude of the ligand effect is much larger for Ir_4. The reversal of PBu_3 and PPh_3 in the order for $Ir_4(CO)_{10}L_2$ can be accounted for in terms of a strengthening of the Ir–CO bonds (ground-state stabilization) by the presence of two weakly π-accepting PBu_3 ligands.

In CO dissociative processes from these iridium clusters, loss of CO from the substituted iridium center(s) would create a situation very similar to mononuclear and dinuclear complexes where the ligand would have the most direct effect on the coordinatively unsaturated transition state. The incoming ligand would not fill the empty coordination site because of steric crowding, and the unsaturation could be transferred by a bridging carbonyl to an unsubstituted iridium center, analogous to our suggested mechanism for $Mn_2(CO)_9L$ (Figure 3).

The reactions of other cluster complexes that have been investigated are consistent with the mechanistic scheme that we have suggested for tetrairidium clusters. The rate acceleration for CO dissociation in triruthenium clusters by PPh_3 is smaller in magnitude than observed for tetrairidium but readily explained as stabilization of the transition state by PPh_3. The labilization by $P(OMe)_3$ in $Co_4(CO)_{12}$ is smaller than expected; perhaps labilization by a more electron-releasing ligand would be larger.

An important feature of these studies of the reactivity of metal clusters is the ability to select or control reactivity of organometallic complexes. As shown in Table IX the reactivity of tetrairidium clusters can be adjusted through a range of 10^3 by changing the ligand environment.

The idea of stabilization of the electron-deficient transition state by electron-donating ligands seems to have wide applicability in substitution of organometallic compexes. Angelici and co-workers offered convincing evidence for stabilization of electron-deficient transition states by electron-donating o-phenanthroline ligands a number of years ago.[50] We have now seen that this simple explanation of reactivity is applicable in mononuclear complexes, dinuclear complexes, and transition-metal clusters. A complete interpretation requires knowledge of site specificity, steric effects in both the ground state and the transition state, and the ground-state bond energies, but the gross effects, especially in

(50) Angelici, R. J.; Jacobson, S. E.; Ingemanson, C. M. *Inorg. Chem.* **1968**, *7*, 2466.

a series of complexes, can be accounted for in terms of a stabilization of the electron-deficient transition state by electron-donating groups.

Multiphoton Mass Spectrometry

EDWARD W. SCHLAG* and HANS J. NEUSSER

Institut für Physikalische und Theoretische Chemie, Technische Universität München, D-8046 Garching, West Germany

Received October 18, 1982 (Revised Manuscript Received February 8, 1983)

With the development of intense, pulsed lasers the absorption of several photons by a single particle became experimentally feasible, and multiphoton absorption has become an interesting method for the study of both atoms and molecules. It has the intriguing possibility of employing visible or near-ultraviolet light, which is readily obtainable, to produce high-energy states otherwise only accessible to vacuum ultraviolet light, which is difficult to produce. In the gas phase the lowest order of multiphoton absorption, two-photon absorption, was first studied with atoms and later with small molecules like nitric oxide[1] and also with polyatomic molecules like benzene.[2]

Since the selection rules of a two-photon process are different from those of a one-photon absorption, this opens up interesting new possibilities for the analysis of molecular spectra and structure, the first novel assignment in the gas phase being that for benzene.[3]

The observation of a two-photon transition can either proceed by detecting the fluorescence from the two-photon excited state or by exciting the molecule from the two-photon state to the ionization continuum with additional photons.[4,5] Such experiments can be carried out in the bulk gas phase or in a molecular beam. Multiphoton absorption to produce ions either via a one-photon or a two-photon state suggests the coupling of this method of ionization to a mass spectrometer. Early work on alkali-metal dimers, which are easily ionized at low energies, pointed to such possibilities.[6]

It was not until 1978 that a detailed mass spectrum was produced from a multiphoton source. Antonov et al. in a study of benzaldehyde and benzophenone used a combination of a fixed-frequency nitrogen and a fixed-frequency hydrogen laser[7] to produce ions at a fixed wavelength. Similarly, Rockwood et al. ionized benzene

with a fixed-frequency KrF laser[8] and obtained an intense mass spectrum. In the same year, however, the full power of multiphoton methods in a mass spectrometer, along with some unexpected features, became clear when variable wavelengths were employed. Schlag et al.[9] as well as Bernstein et al.[10] revealed in different ways some of the main features of multiphoton mass spectrometry. Schlag et al.[11] demonstrated that the isotopic species mono-^{13}C-benzene can be preferentially ionized in a natural isotopic mixture by shifting the wavelength by 1.6 cm^{-1} from the absorption band of light benzene. This demonstrated that trace components in a mixture can be ionized without ionizing the major components if the intermediate-state spectrum shows sharp features at a resolution of 1 cm^{-1}. In general, the optical enhancement in a mass spectrometer can be obtained if the absorption coefficient of the various components differs at any chosen wavelength, which is also given for most molecules with broad absorption spectra. In further work they showed that the laser intensity can be adjusted so that only a (very strong) parent ion peak appears. This exclusive parent ionization is difficult to produce in conventional mass spectrometry, and soft ionization appears to be possible for all molecules that can be ionized in a two-photon ionization process with a real intermediate state that is resonant with the energy of one photon. For state-

Edward W. Schlag was born in Los Angeles, CA, in 1932. He received his B.S. from Occidental College and his Ph.D. from the University of Washington. In 1958 he did postdoctorate work at the University of Bonn, Germany; in 1959 he was a Research Scientist at Films Department at E. I. duPont de Nemours. He then joined the faculty of Northwestern University, where he became Professor of Chemistry in 1969. In 1971 he moved to the Technical University, Munich, Germany, as Professor of Physical Chemistry, and has served as Dean of the Faculty of Chemistry, Geology and Biosciences.

Hans Jürgen Neusser was born in Troppau in 1943. In 1971 he received the Dr.rer.nat. degree in Physics at Technische Universität, München, Germany, and in 1977 he received the Dr.rer.nat.habil. in Chemistry from the same institution. Since 1979 he has been Professor for Physical Chemistry and Laser Spectroscopy at the Chemistry Department of Technische Universität, München.

(1) R. G. Bray, R. M. Hochstrasser, and J. E. Wessel, *Chem. Phys. Lett.*, **27**, 167 (1974).

(2) R. M. Hochstrasser, J. E. Wessel, and H. N. Sung, *J. Chem. Phys.*, **60**, 317 (1974).

(3) L. Wunsch, H. J. Neusser, and E. W. Schlag, *Chem. Phys. Lett.*, **31**, 433 (1975).

(4) G. Petty, C. Tai, and F. W. Dalby, *Phys. Rev. Lett.*, **34**, 1207 (1975).

(5) P. M. Johnson, *J. Chem. Phys.*, **62**, 4562 (1975); *Acc. Chem. Res.*, **13**, 20 (1980); P. M. Johnson and C. E. Otis, *Ann. Rev. Phys. Chem.*, **32**, 139 (1981).

(6) D. L. Feldman, R. K. Lengel, and R. N. Zare, *Chem. Phys. Lett.*, **52**, 413 (1977); A. Hermann, S. Leutwyler, E. Schumacher, and L. Wöste, *Chem. Phys. Lett.*, **52**, 418 (1977); E. W. Rothe, B. P. Mathur, and G. P. Reck, *ibid.*, **53**, 74 (1978).

(7) V. A. Antonov, I. N. Knyazev, V. S. Letokhov, V. M. Matiuk, V. G. Morshev, and V. K. Potapov, *Opt. Lett.*, **3**, 37 (1978).

(8) S. Rockwood, J. P. Reilly, K. Hohla, and K. L. Kompa, *Opt. Commun.*, **28**, 175 (1979).

(9) U. Boesl, H. J. Neusser, and E. W. Schlag, *Z. Naturforsch. A*, **33**, 1546 (1978).

(10) L. Zandee and R. B. Bernstein, *J. Chem. Phys.*, **70**, 2574 (1979); **71**, 1359 (1979).

(11) U. Boesl, H. J. Neusser, and E. W. Schlag, *J. Am. Chem. Soc.*, **103**, 5058 (1981).