Table I. Ligand Substitution on the Decacarbonyls of Group 7

$M_2(CO)_{10}$	L	product	kinetics (order in $M_2(CO)_{10}$)	ref
$Mn_2(CO)_{10}$	PPh_3, $P(OPh)_3$, etc.	$Mn_2(CO)_9L$ and $Mn_2(CO)_8L_2$	1st order, several $t_{1/2}$	3
$Mn_2(CO)_{10}$	PPh_3	$Mn_2(CO)_9PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$	1st order, $3t_{1/2}$	4
$Re_2(CO)_{10}$	PPh_3	$Re_2(CO)_8(PPh_3)_2$	1st order, $2\text{-}3t_{1/2}$	5
$Tc_2(CO)_{10}$	PPh_3	$Tc_2(CO)_9PPh_3$ and $Tc_2(CO)_8(PPh_3)_2$	1st order, $3t_{1/2}$	6
$MnRe(CO)_{10}$	PPh_3	$(CO)_5MnRe(CO)_4PPh_3$	1st order, $3t_{1/2}$	6
$MnRe(CO)_{10}$	PPh_3, $P(OPh)_3$, PBu_3	$(CO)_5MnRe(CO)_4L$ and $MnRe(CO)_8L_2$	1st order, $3t_{1/2}$	2

O_2 would give exactly the characteristics noted in the preceding quotation and would account for the pressure dependence of O_2.[3–8] Poë has never commented on the equilibrium concentration of O_2 in decalin at these high temperatures.

In the preceding two paragraphs I have argued that ligand substitution reactions on $M_2(CO)_{10}$ are different from the other reactions which Poë has discussed in the preceding paper and that the thermal decompositions are experimentally difficult to interpret. I would now like to again present the evidence for CO dissociation and against homolytic fission in ligand substitutions on $MnRe(CO)_{10}$.[2] The rate law and dependence on the nucleophilicity of the entering ligand are analogous to those observed for substitutions on $Cr(CO)_6$ and $Mo(CO)_5Am$, which occur by ligand dissociations of an interchange type.[2,18–20] Inhibition of the rate by CO is also consistent with a CO-dissociative mechanism. The conclusive evidence against a radical mechanism is the product distribution. No homodimetallic complexes are observed (even as intermediates)[2] during the course of the reaction of $MnRe(CO)_{10}$ with phosphines and phosphites. For the observed product distribution to be obtained by homolytic fission of the Mn–Re bond, the manganese isomer, $L(CO)_4MnRe(CO)_5$, would have to rearrange to the rhenium isomer, $(CO)_5MnRe(CO)_4L$, under the reaction conditions.[2,21] This reaction does not occur.

$$L(CO)_4MnRe(CO)_5 \nrightarrow (CO)_5MnRe(CO)_4L \qquad (5)$$

The failure of this isomerization to occur under the reaction conditions rules out the radical mechanism for thermal ligand substitution.[21] The failure to observe homodimetallic complexes also rules out the radical mechanism in the absence of an unusual selectivity in recombination of radicals. In recent experiments of the 17-electron species $\cdot CpFe(CO)PPh_3$ with $Mn_2(CO)_{10}$, we observed eight products from radical recombinations during the course of the room-temperature reaction, suggesting that there is little selectivity in radical recombinations.[22,23] This is consistent with the observations that a variety of 17-electron complexes undergo recombinations at diffusion-controlled rates.[24]

In this paper I have tried to clarify the issue of reaction mechanisms of the group 7 carbonyl dimers. I have shown (1) the simple substitution reactions are different from the other reactions that Poë has studied, (2) there are substantial *experimental* problems that could lead to the poor kinetics seen in the decomposition reactions, and (3) there is *no* evidence that is inconsistent with a CO-dissociative process for the thermal ligand substitution reactions of the group 7 decacarbonyls.

Note Added in Proof. Substitution reactions on $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ occur between 100–120 and 130–150 °C, respectively. Recent work has shown that reaction to $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ does not lead to $MnRe(CO)_{10}$ at 130 °C.[27] We have confirmed this failure to react at 150 °C under a CO atmosphere in toluene. In 48 h no $MnRe(CO)_{10}$ was seen and no decomposition of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ was observed. These observations show that $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ cannot both undergo substitution reactions by metal–metal bond homolysis.

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(18) (a) Darensbourg, M. Y.; Darensbourg, D. J.; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *95*, 3127. (b) Ewen, J.; Darensbourg, D. J. *Ibid.* **1975**, *97*, 6874.

(19) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082.

(20) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.

(21) Both the manganese and the rhenium isomers grow in absorbance, reach a constant absorbance, and then decrease at the end of the substitution reaction, while the bissubstituted complex continues to grow throughout the reaction. If a radical mechanism is occurring, then the formation reactions must be equilibria (the growth and then decrease in concentration mandate a further reaction of $(CO)_5MnRe(CO)_4L$ and $L(CO)_4MnRe(CO)_5$, which requires Mn–Re bond fission for the radical mechanism) to give this behavior:

$$\cdot Re(CO)_4L + \cdot Mn(CO)_5 \rightleftharpoons (CO)_5MnRe(CO)_4L$$

$$\cdot Mn(CO)_4L + \cdot Re(CO)_5 \rightleftharpoons L(CO)_4MnRe(CO)_5$$

For the observed relative amounts of manganese and rhenium isomers to be obtained, the first equilibrium must lie to the right and the second to the left.[2] With the assumption that the 17-electron species undergo rapid ligand transfer,[22–26] the manganese isomer must rearrange to the rhenium isomer under the reaction conditions for a homolytic fission mechanism to operate. There was no trace of $(CO)_5MnRe(CO)_4L$ observed in the isomerization.

(22) Wong, A.; Sonnenberger, D.; Rees, W.; Atwood, J. D. "Abstracts of Papers" Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, LA, Dec 1980; American Chemical Society: Washington, DC, 1981; INOR 307.

(23) Wong, A.; Atwood, J. D., submitted for publication.

(24) Brown, T. L.; Forbes, N. P.; Wegman, R. W.; Paper No. 239, Division of Inorganic Chemistry, Second Chemical Congress of the North American Continent, Las Vegas; 1980.

(25) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527.

(26) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095.

(27) Schmidt, S.; Basolo, F.; Trogler, W., manuscript in preparation.

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Response to Preceding Correspondence

Sir:

Atwood has not addressed the fundamental question of why, if decomposition under O_2 occurs by a path quite different from substitution, clean substitution of $MnRe(CO)_{10}$ still occurs even under O_2 and at the same rate as substitution or decomposition individually. He also states that decomposition reactions occurring at least-than-limiting rates are "not half order". On the contrary for $Mn_2(CO)_{10}$ they vary continuously from first order down to clear half order as $[O_2]$ decreases and $[Mn_2(CO)_{10}]$ increases. The orders were determined from the dependence of initial rates on initial concentrations, i.e., under conditions where interference from products would be expected to be minimal and where any depletion of $[O_2]$ has had no time to occur. With allowance for the acknowledged complexity of the decomposition reactions, the quantitative agreement with the homolytic fission mechanism has to be considered excellent. Since the decomposition and substitution reactions must proceed by the same rate-limiting step, it is surely incumbent on those who favor the CO-dissociative mechanism to present

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at least an equally satisfactory *quantitative* fit of the data to that mechanism over the very wide ranges of [complex], [O_2], and [CO] used. This has still not been done.

All this is not to say, of course, that further testing of the validity of the homolytic fission mechanism is not required. More experiments designed specifically to show different results for the different possible mechanisms would clearly be important, but it would equally clearly be unwise at this stage to dismiss the homolytic fission mechanism out of hand.

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Anthony Poë

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Bent's Rule: Energetics, Electronegativity, and the Structures of Nonmetal Fluorides

Sir:

Bent's rule,[1] "*atomic s character tends to concentrate in orbitals that are directed toward electropositive groups and atomic p character tends to concentrate in orbitals that are directed toward electronegative groups*", has proved to be useful in explaining many aspects of the structural chemistry of organic and inorganic compounds.[1,2a] Furthermore, it is often cited as good chemical "horse sense" in theoretical studies.[3] Despite its success in the simple rationalization of molecular structures, little discussion of the physical basis of the effect has appeared. Bent[1] suggested, on the basis of perturbation theory, that isovalent hybridization should occur to transfer more s character to the electropositive-bonding orbital, since that transfer would maximize the bonding energy: The electrons bonding the electropositive element would be lowered in energy more than those bonding the electronegative element would be raised.

Grim et al.[4] have reported an apparent exception to Bent's rule, and, on the basis of this and other considerations, the Rule was modified in terms of orbital energy matching and overlap: "*The p character tends to concentrate in orbitals with weak covalency (arising from either electronegativity or overlap considerations), and s character tends to concentrate in orbitals with strong covalency (matched electronegativities and good overlap)*".[2b] The present communication suggests an extension and amplification of this point of view that, although not conflicting with the views of previous workers, provides a simple rationale for the operation of Bent's rule in molecules with highly electronegative substituents, provides an explanation for the s affinity of lone pairs (LP) in terms of energetics and Bent's rule, and furthermore helps rationalize the structures of certain nonmetal fluorides.

Consider the series of phosphorus fluorides, XPF_3 (where X = LP, BH_3, S, etc.), their respective FPF bond angles, and the corresponding s character of the X- and F-directed orbitals on the phosphorus atom (P_X and P_F, respectively):

compd	FPF, deg	% s P_F	% s P_X
$:PF_3$	97.8[4]	11.9	64.1
H_3BPF_3	100[5]	15	55
SPF_3	100.3[6]	15.2	54.5
OPF_3	101.3[6]	16.4	50.8
PF_4^+	109.5	25.0	25.0

Gillespie[8] has suggested that a lone pair can be considered to be a "substituent" with an effective electronegativity of zero since the lone pair is under the complete control of a single nucleus. Thus the above series contains substituents on the $-PF_3$ moiety ranging in electronegativity from 0 to 4 (Pauling scale). The FPF bond angle (and the s character of the fluorine-bonding phosphorus orbitals, P_F) increases as the amount of s character devoted to the fourth substituent (LP, B, S, O, F) decreases, as expected for isovalent hybridization according to Bent's rule. Boron behaves as a somewhat *more* electronegative atom (FPF angle larger) than expected because of the formal positive charge that it induces on the phosphorus atom. On the other hand, the oxygen atom appears to be somewhat *less* electronegative (as interpreted from the bond angles) than expected because of the extra VSEPR effect of the O=P double bond (see below).[2c,8,9] Note that the formally isoelectronic, but non-double-bonded, ONF_3 has bond angles closely approaching those of a tetrahedral molecule.[9]

Consider the following limits for the s character in the fluorine-bonding phosphorus orbitals of the compounds listed above. At the covalent or high-s limit (PF_4^+), all of the orbitals are identical sp^3 (te) hybrid orbitals. The change from the ground state of the nonbonded phosphorus atom to that in the fluorophosphonium ion, PF_4^+, will be $3s^2\ 3p^1\ 3p^1\ 3p^1 \rightarrow 3s^1\ 3p^1\ 3p^1\ 3p^1 + e$. The ionic or low-s limit (X = lone pair) is for the wave function corresponding to the ionic contributing structure in the resonance

$$:PF_3 \leftrightarrow :P^{+3} + 3F^-$$

with a change from ground state to the valence state of $3s^2\ 3p^1\ 3p^1\ 3p^1 \rightarrow 3s^2\ 3p^0\ 3p^0\ 3p^0$. In this limit, it is energetically favorable to ionize the higher energy 3p electrons and allow the lone pair to consist solely of the lower energy 3s pair. A configuration $3s^1\ 3p^1\ 3p^0\ 3p^0$ would represent an excited state and contribute little to the ionic structure above. The energies involved are thus closely related to those of unsymmetrical hybridization.[2d] While it might be argued that complete ionization of the 3p electrons is an unrealistic limit in a predominantly covalent molecule, the partial ionization potential–electron affinity energy of covalent molecules is an important component of total bonding energy.[1,11]

Some interesting consequences of the energies associated with Bent's rule are shown by various nonmetal fluorides. The appropriate application of Bent's rule in conjunction with the VSEPR rules of Gillespie[8,9] provides insight into the detailed structure of these molecules. In the following discussion, the *z* axis is taken as the rotational axis of highest order in the trigonal bipyramid and square pyramid, the *x* axis as the second axis lying in the plane of the paper, and the *y* axis as the axis perpendicular to the paper. In accordance with common usage, axial substituents shall be those lying along the *z* axis, and equatorial substituents shall be those lying in the *xy* plane.

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(1) H. A. Bent, *J. Chem. Educ.*, **37**, 616 (1960); *J. Chem. Phys.*, **33**, 1258 (1959); 1260 (1960); *Chem. Rev.*, **61**, 275 (1961).

(2) J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd ed., Harper & Row, New York and San Francisco, 1978: (a) pp 145–147, 206, 227; (b) p 146; (c) p 205; (d) pp 143–145; (e) pp 201–202; (f) p 212; (g) p 188, 4.7.

(3) For example, see J. P. Foster and F. Weinhold, *J. Am. Chem. Soc.*, **102**, 7211 (1980).

(4) S. O. Grim, H. J. Plastas, C. L. Huheey, and J. E. Huheey, *Phosphorus Relat. Group V Elem.*, **1**, 61, (1971).

(5) Y. Morino, K. Kuchitsu, and T. Moritani, *Inorg. Chem.*, **8**, 867 (1969).

(6) R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, **46**, 357 (1967).

(7) T. Moritani, K. Kuchitsu, and Y. Morino, *Inorg. Chem.*, **10**, 344 (1971).

(8) R. J. Gillespie, "Molecular Geometry", Van Nostrand-Reinhold, London, 1972, pp 55–56.

(9) K. O. Christe and H. Oberhammer, *Inorg. Chem.*, **20**, 296 (1981).

(10) N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.*, 213 (1966); E. C. Curtis, D. Pilipovich, and W. H. Moberly, *J. Chem. Phys.*, **46**, 2904 (1967); W. B. Fox, J. S. MacKenzie, E. R. McCarthy, J. R. Holmes, R. F. Stahl, and R. Juurik, *Inorg. Chem.*, **7**, 2064 (1968).

(11) R. S. Evans and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **32**, 777 (1970).

0020-1669/81/1320-4033$01.25/0