Mechanistic Studies of Phosphorus–Oxygen Bond Cleavages in Group 7 Dinuclear Complexes of 2-Pyridyl Dimethylphosphinite

**David B. Collum,* Jeffrey A. Klang, and Randall T. Depue**

Contribution for the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853. Received August 21, 1985

Abstract: Dinuclear chelates *fac*-L₂Re(CO)₃[M(CO)₅] (L₂ = 2-pyridyl dimethylphosphinite, **2**, M = Re; **3**, M = Mn) rearranged in benzene at 80 °C to provide the corresponding (CO)₄Re(μ-OPYR)(μ-PMe₂)M(CO)₄ derivatives **5** (M = Re) and **6** (M = Mn) in 95 and 94% yield, respectively. The rearrangements exhibited first-order kinetics to >3 half-lives and displayed the following kinetic parameters: M = Re, $\Delta H^{\ddagger}$ = 24.2 ± 1.8 kcal/mol and $\Delta S^{\ddagger}$ = −10 ± 5 eu; M = Mn, $\Delta H^{\ddagger}$ = 22.2 ± 0.7 kcal/mol and $\Delta S^{\ddagger}$ = −11 ± 2 eu. The reaction rates and the products formed were unaffected by added CO, methylating agents, or triphenylphosphine. In the presence of carbon tetrachloride, the rearrangements afforded mixtures of the P–O cleavage products (**5** or **6**) and *fac*-(CO)₆L₂ReCl. Crossover studies showed the rearrangements of **2** and **3** to occur with statistically significant inter- and intramolecular components. The results are discussed in light of mechanisms involving CO dissociation, homo- and heterolytic metal–metal bond cleavage, and a novel dyotropic rearrangement.

Reports of the cleavage of phosphorus–carbon bonds by transition metals have received considerable attention recently because of their potential roles in the deactivation of homogeneous catalysts.[1] In contrast, the corresponding cleavages of phosphorus–oxygen bonds in transition-metal phosphite complexes have been detailed on only a few occasions.[2] Presumably this derives, in part, from the large (≥80 kcal/mol) P–O bond energies.[3] Nonetheless, we recently reported a notably facile cleavage of the P–O bond of 2-pyridyl dimethylphosphinite (**1**) by CpCo-(CH₂=CH₂)₂.[4] In this paper we describe mechanistic studies of similar cleavages occurring on group 7 dinuclear frameworks.

Results

Starting Materials and Products. During studies of the chemistry of complexes of ligand **1**,[5] we prepared dinuclear complexes **2** and **3** as follows. Heating (CO)₅ReBr[6] with 1.0 equiv of ligand **1** in toluene for 15 min at 110 °C afforded fac isomeric complex **4** in an 88% yield after recrystallization. The fac stereochemistry was evident from the distinct resonances in the ¹³C and ¹H NMR spectra of **4** for the diastereotopic methyl groups. When **4** was treated with NaRe(CO)₅[7] in THF at 25 °C, dirhenium chelate **2** could be isolated in a 49% yield after recrystallization. Again, diastereotopic methyl resonances demonstrated the retention of the fac stereochemistry. The ³¹P NMR spectrum of **2** showed a single resonance at 139.6 ppm. Heterodinuclear chelate **3** could be prepared in a 44% yield after recrystallization by treatment of **4** with (CO)₅MnNa[8] in THF. The spectroscopic analysis of **3** proceeded analogously to **2**.
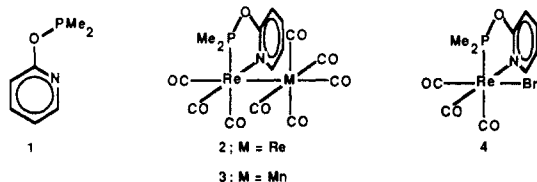
Warming **2** at 80 °C in benzene-d_6 effected a clean replacement of the ³¹P NMR resonance of **2** at 139.6 ppm by a dramatically upfield shifted resonance at −68.1 ppm; no intermediate resonances were observed. Bridging phosphide **5** was isolated in a 95% yield after chromatography as a slightly air sensitive, colorless crystalline solid. The ¹³C NMR spectrum of **5** revealed an absence of phosphorus coupling with the pyridyl carbons, suggesting the P–O bond had been cleaved. The chemical shift of the phosphorus resonance in the ³¹P NMR spectrum implicated the absence of a Re–Re bond.[9] Comparison of the ¹H NMR spectrum of **5** with uncoordinated **1** (as well as mono- and bidentate complexes of **1**) supported the assigned bridging alkoxide structure rather than the more common[10] η^2-(N,O) form of the hydroxypyridine moiety. Due to the stereocenter defined by the bridging oxygen atom, the methyl groups on phosphorus were diastereotopic and, hence, became inequivalent in the slow exchange ¹H NMR spectrum (−80 °C). The ³¹P NMR spectrum was invariant from −80 to 120 °C. An elemental analysis was consistent with the overall formulation.

Similarly, heating **3** in benzene-d_6 effected clean replacement of the resonance of **3** at 143.0 ppm by a single upfield ³¹P resonance at −20.5 ppm. Heteronuclear bridging phosphide **6** was isolated after chromatography in a 94% yield and characterized by the same spectroscopic techniques as described above.

1

2; M = Re
3; M = Mn

4

2 (or 3) →(80 °C)→

5; M = Re, 95% yield
6; M = Mn, 94% yield
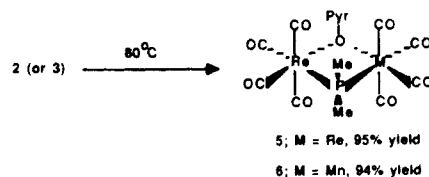
Attempts to prepare dinuclear complexes **7** and **8** met with limited success. Fac isomeric chelate **9** was prepared in an 80% yield after recrystallization by heating (CO)₅MnBr[11] and ligand **1** in toluene at 110 °C for 10 min. Treatment of **9** with excess NaMn(CO)₅ for extended reaction times produced only low percent conversions. The crude ³¹P NMR spectrum exhibited a singlet at 196.7 ppm consistent with structure **7**. However, attempts to isolate pure **7** by recrystallization, gel permeation chromatography, or flash chromatography were uniformly un-

(1) Garrou, P. E. *Adv. Organomet. Chem.* **1984**, *23*, 95.

(2) Day, V. W.; Tavanaiepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657. Duttera, M. R.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2907. Reagan, W. J.; Burg, A. B. *Inorg. Nucl. Chem. Lett.* **1971**, *7*, 741. Orpen, A. G.; Sheldrick, G. M. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1992. Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43.

(3) Emsley, J.; Hall, D. "The Chemistry of Phosphorus"; Harper and Row: New York, 1976; p 35. Kochi, J. K. "Free Radicals"; Wiley: New York, 1973; Vol. II, p 598.

(4) Collum, D. B.; DePue, R. T.; Klang, J. A. *Organometallics*, in press.

(5) Depue, R. T.; Collum, D. B.; Ziller, J. W.; Churchill, M. R. *J. Am. Chem. Soc.* **1985**, *107*, 2131.

(6) King, R. B.; Reimann, R. H. *Inorg. Chem.* **1976**, *15*, 179.

(7) Darst, K. P.; Lukehart, C. M.; Warfield, L. T.; Zeile, J. V. *Inorg. Synth.* **1978**, *20*, 201.

(8) Lukehart, C. M.; Torrence, G. P.; Zeile, J. V. *Inorg. Synth.* **1978**, *18*, 57.

(9) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. *Organometallics* **1983**, *2*, 470. Rosen, R. P.; Hoke, J. B.; Whittle, R. R.; Geoffroy, G. L.; Hutchinson, J. P.; Zubieta, J. A. *Organometallics* **1984**, *3*, 846. Peterson, J.; Stewart, R. P., Jr. *Inorg. Chem.* **1980**, *19*, 186. Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Rosenberg, S.; Whittle, R. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 5934.

(10) Leading references: Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A. *Inorg. Chem.* **1984**, *23*, 4030. Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

(11) Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 160.

Table I. Observed First-Order Rate Constants for the Rearrangements of 2 and 3

chelate 2[a]		chelate 3[b]	
temp, °C	$10^5 k_{obsd}$, s^{-1}	temp, °C	$10^5 k_{obsd}$, s^{-1}
60.3	0.72 ± 0.11	43.0	0.95 ± 0.08
62.4	0.95 ± 0.09	56.1	3.69 ± 0.15
73.1	2.78 ± 0.43	67.1	13.1 ± 0.56
84.0	6.62 ± 0.87	71.6	24.7 ± 2.4
84.0	6.84 ± 0.74	75.2	31.8 ± 1.5
84.9	5.89 ± 0.58	80.3	46.7 ± 4.1
86.8	6.08 ± 0.28	86.9	67.7 ± 8.6
96.4	22.8 ± 2.5	95.0	147.9 ± 32.0
100.5	48.2 ± 4.7		
100.5	24.3 ± 1.6		
112.0	146.9 ± 18.0		

[a] Run 0.027 M in toluene-d_8. [b] Run 0.031 M in toluene-d_8.

**Table II.** Kinetic Parameters for the Thermal Rearrangements of 2 and 3[a]

compd	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol·deg K)
2	24.2 ± 1.8	−10 ± 5
3	22.2 ± 0.7	−11 ± 2

[a] Conditions and rate constants are listed in Table I and Figures 1 and 2.

Table III. Solvent Rate Effects

solvent	$10^5 k_{obsd}$, s^{-1}	k_{rel}
For Thermolysis of 2[a]		
benzene[b]	1.08 ± 0.14	1.0
1:1 benzene/THF[b]	1.71 ± 0.17	1.6
1:1 benzene/CH$_3$CN[b]	1.62 ± 0.17	1.5
For Thermolysis of 3[c]		
benzene[a]	2.63 ± 0.06	1.0
1:1 benzene/THF[a]	1.33 ± 0.04	0.5
1:1 benzene/CH$_3$CN[a]	1.75 ± 0.01	0.7

[a] Run at 67.3 °C, [2] = 0.027 M. [b] Ratio of solvents by volume. [c] Run at 54.0 °C, [3] = 0.031 M.

satisfactory. If the crude reaction product was heated at 70 °C in C$_6$D$_6$ for 24 h, the resonance at 196.7 ppm attributable to 7 was replaced by a new resonance at 28.7 ppm. (The other resonances remained invariant.) Flash chromatography afforded phosphide 10 (30% overall yield from 9) as an orange oil, with spectral properties resembling those of 2 and 3.
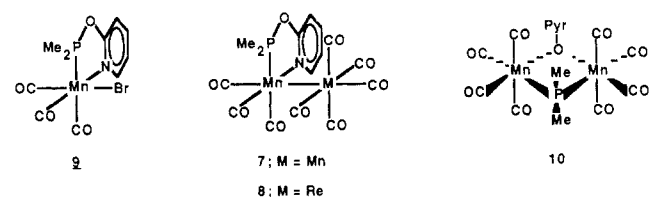
Similarly, chelate 8 could not be isolated from the coupling of bromide 9 and NaRe(CO)$_5$. Thermolysis of the crude reaction mixture from the coupling furnished phosphide 6 in a 27% yield after chromatography.

Rate Studies. The isomerizations of 2 and 3 were monitored by ^{1}H NMR spectroscopy and shown to follow first-order kinetics to >3 half-lives. Reaction rates monitored over a 52 °C temperature range (Table I) afforded linear plots of ln (k_{obsd}/T) vs. $1/T$ (Figures 1 and 2). Kinetic Eyring parameters (Table II) were calculated by a *nonlinear*, weighted least-squares fit.[12] The $\Delta S^{\ddagger}$ for both rearrangements were significantly negative values and were equal within experimental error. The faster reaction rates of heteronuclear chelate 3 were traced to the smaller $\Delta H^{\ddagger}$ term.

No rate inhibitions (<5%) were detected when the thermolyses of 2 or 3 were run under 1 atm of CO. The rates of the rear-

(12) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96, 162.
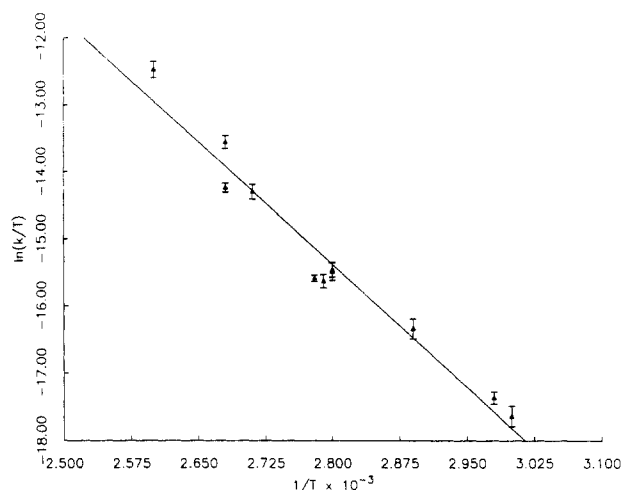
Figure 1. Rate of rearrangement of chelate 2 as a function of temperature. Reactions were run 0.027 M in toluene-d_8. Calculated kinetic parameters are listed in Table II. Measured rate constants are listed in Table I.
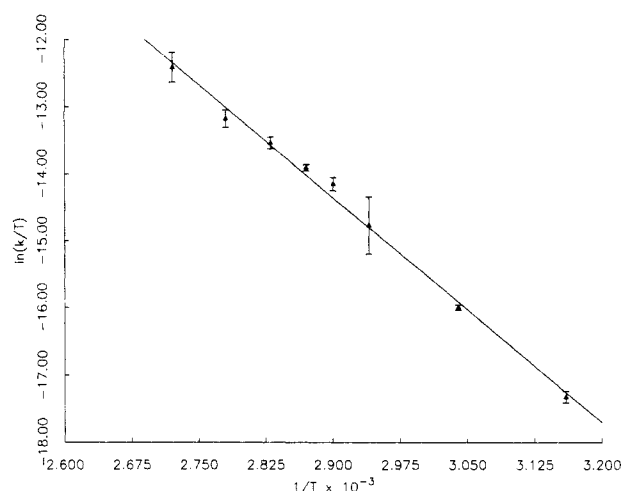
Figure 2. Rate of rearrangement of chelate 3 as a function of temperature. Reactions were run 0.031 M in toluene-d_8. Calculated kinetic parameters are listed in Table II. Measured rate constants are listed in Table I.

rangements were also determined in neat C$_6$D$_6$, 1:1 by volume C$_6$D$_6$/THF, and 1:1 by volume C$_6$D$_6$/acetonitrile (Table III). The effects of solvent polarity and coordinating ability on the reaction rates were minimal.

Trapping Studies: PPh$_3$. When 2 was heated in the presence of 1.0 equiv of PPh$_3$, ^{31}P and ^{1}H NMR analysis showed only bridging phosphide 5. Upon extended heating, monosubstitution of 5 occurred to produce phosphide 11 in 38% yield.
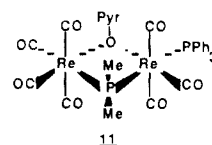
Trapping Studies: Methylating Agents. In an attempt to trap intermediate (η^2-1)(CO)$_3$Re$^+$/−M(CO)$_5$ species, chelates 2 and 3 were heated in a 6:1 (by *volume*) mixture of C$_6$D$_6$:MeI. Monitoring by ^{1}H NMR revealed <5% of the MeM(CO)$_5$[13] methylation products (M = Re or Mn) as shown by comparison with authentic samples. Similarly, rearrangement in the presence of dimethyl sulfate or methyl fluorosulfonate (5 equiv) also failed

(13) Hieber, W.; Braun, G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1959**, *14*, 132. Clossen, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598.
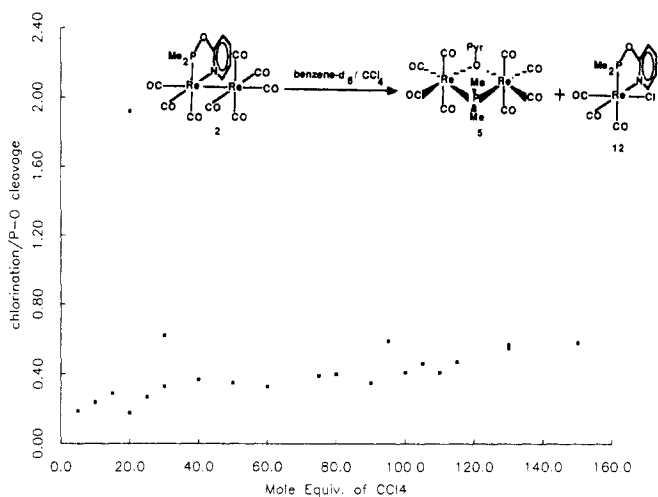
Figure 3. A plot of the relative rates of chlorination and phosphorus–oxygen bond cleavage (**5:12**) formed during the rearrangement of **2** as a function of the number of molar equivalents of carbon tetrachloride. The reactions were run 0.027 M in benzene-d_6/CCl$_4$ at 80 °C.

Figure 4. A plot of the relative rates of chlorination and phosphorus–oxygen bond cleavage (**6:12**) formed during the rearrangement of **3** as a function of the number of molar equivalents of carbon tetrachloride. The reactions were run 0.027 M in benzene-d_6/CCl$_4$ at 80 °C.
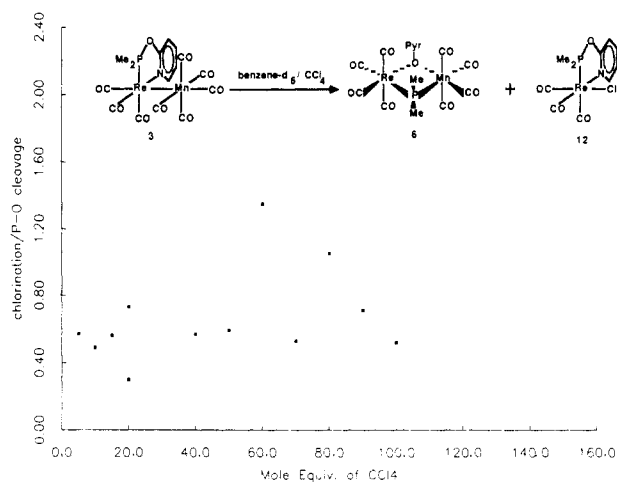
to provide any detectable methylation products. These results, in combination with the minimal solvent effects, militate against metalates as intermediates en route to the bridging phosphide products.

Trapping Studies: CCl$_4$. The thermal rearrangements of **2** in CCl$_4$/benzene mixtures furnished phosphide **5** and metal chloride **12** (eq 1); analogous thermolyses of **3** produced mixtures of **6** and
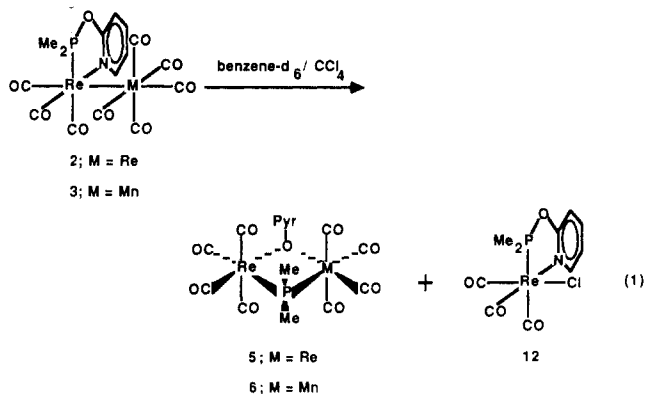
12. The chlorination/P–O cleavage ratios were monitored as a function of CCl$_4$ concentration (Figures 3 and 4). Despite precautionary measures, including rigorous solvent degassing,

Scheme I
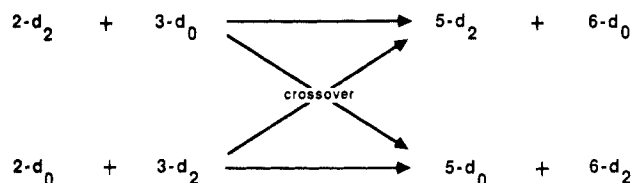
exclusion of light, precise temperature control, and careful solvent purification, the data were considerably scattered in both cases.

Several salient observations were made during our attempts to find the source of the fluctuations. From the ratios, we calculated the chlorination reaction orders in CCl$_4$ to be 0.18 ± 0.10 and 0.13 ± 0.10 for **2** and **3**, respectively.[14] Within the large experimental error imparted by the scatter, the chlorinations were essentially zero order in CCl$_4$. This is consistent with the frequently cited propensity for CCl$_4$ to efficiently scavenge metal radicals.[15]

In an effort to find a more dependable scavenger of the (presumed) intermediate metal-centered radicals, we discovered that hexachloroethane (C$_2$Cl$_6$) reacted with chelates **2** and **3** markedly more rapidly (25 °C, 0.5 and 12 h, respectively) than did CCl$_4$. If the chlorinations of **2** and **3** by both CCl$_4$ and C$_2$Cl$_6$ were occurring via a post-rate-determining radical scavenging, the rates should have been independent of the reagent used (zero order). Since there is little evidence that **2** and **3** could be undergoing facile thermally-induced metal–metal bond homolyses at ambient temperatures,[16] we conclude that the C$_2$Cl$_6$ chlorinations must proceed by a different mechanism.

In 1977, Kochi and Nugent reported that the reaction of mercury dialkyls with C$_2$Cl$_6$ appeared to proceed by a radical chain mechanism.[17] In addition, the C–Hg bond chlorinations using CCl$_4$ produced C$_2$Cl$_6$ as a byproduct from the coupling of CCl$_3$ radicals. Clearly, the C$_2$Cl$_6$ generated during the course of rearrangements of **2** and **3** would contribute to the fluctuations in the chlorination/P–O cleavage ratios and could be the predominant source of metal halide **12**.

The chloride **12** did *not* necessarily arise from innocent scavenging of a thermally generated metal radical. Furthermore, thermolyses of chelates **2** and **3** in the absence of CCl$_4$ did *not* produce the M$_2$(CO)$_{10}$ parent complexes or phosphine-containing by-products that should have resulted from coupling of two M(CO)$_5$ radicals. The 94–95% yields of bridging phosphides **5** and **6** readily account for the mass balance. Therefore, it was not clear whether metal–metal bond homolyses occurred even to a limited extent during the rearrangements. Accordingly, we carried out several crossover experiments.

Crossover Studies. Rearrangement of **2** in the presence of Mn$_2$(CO)$_{10}$ provided phosphide **5** to the exclusion of **6** that would have resulted from incorporation of an Mn(CO)$_5$ fragment. The analogous rearrangement of **3** in the presence of Re$_2$(CO)$_{10}$ produced exclusively noncrossover product **6**. Therefore, if the parent M$_2$(CO)$_{10}$ complexes had been formed during the course of the thermolyses, they could not have escaped detection by re-entering the reaction pathway.

A second crossover experiment was designed as illustrated in Scheme I. Deuterated starting materials **2**-d_2 and **3**-d_2 were

(14) (a) The orders in CCl$_4$ were obtained from the equations

$$k_{obsd} = k'[Y]^Z$$

$$\ln k_{obsd} = \ln k' + Z \ln[Y]$$

(b) Frost, A.; Pearson, R. In "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; Chapter 3.

(15) Herrick, R. S.; Herrinton, T. R.; Walker, H. W.; Brown, T. L. *Organometallics* **1985**, *4*, 42 and references cited therein.

(16) Coville, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1984**, *105*, 2499. Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822. Pöe, A.; Sekhar, C. *J. Chem. Soc., Chem. Commun.* **1983**, 566. Marcomini, A.; Pöe, A. *J. Chem. Soc., Dalton Trans.* **1984**, 95.

(17) Nugent, W. A.; Kochi, J. K. *J. Organomet. Chem.* **1977**, *124*, 349.

2336 *J. Am. Chem. Soc., Vol. 108, No. 9, 1986*

Collum et al.

prepared from deuterated ligand **1**, which, in turn, was prepared from Me$_2$PCl[18] and 3,5-dideuterio-2-hydroxypyridine[19] as described previously.[5] In order to observe crossover, the rearrangements of **2** and **3** must occur at the same time. In practice, to account for the relative rates of P–O bond cleavage and to ensure a significant statistical bias favoring crossover, a 50-fold excess of **3** was employed. The extent of crossover was determined by using field ionization mass spectrometry (FIMS) by monitoring the peaks of **5**-d_0 at 749 (^{185}Re–^{185}Re), 751 (^{185}Re–^{187}Re), and 753 (^{187}Re–^{187}Re) superimposed upon the corresponding peaks of **5**-d_2 at 2 mass units higher.[20,21]

In the event, heating at 1:50 mixture of **2**-d_0 and **3**-d_2 in C$_6$D$_6$ at 80 °C for 40 h afforded a 3:2 mixture of **5**-d_0 and **5**-d_2. The complementary experiment using a 1:50 mixture of **2**-d_2 and **3**-d_0 yielded a 2:3 mixture of **5**-d_0 and **5**-d_2. Because of the dramatic statistical bias favoring crossover, the 3:2 ratio of crossover: noncrossover products reflects the presence of both *inter-* to *intra*molecular components of the rearrangements. Control experiments demonstrated that mixtures of the homodinuclear phosphides **5** and **10** were not in equilibrium with heteronuclear phosphide **6**. Whether the crossover products arose from metal–metal bond cleavages or simply exchanges of the d_0 and d_2 pyridyloxy fragments could not be determined.

Photochemical Studies. When chelate **2** in toluene-d_8 was photolyzed by using a 250-W sunlamp with monitoring by ^{31}P NMR spectroscopy, we observed reactivities consistent with the scenario detailed in eq 2. Thus, photolysis of **2** for 1 h at −75
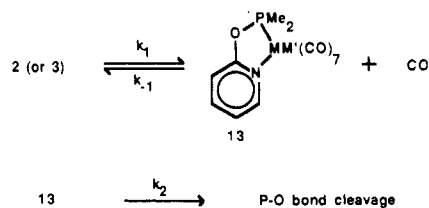
(2)
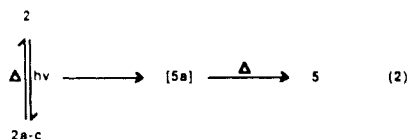
°C provided three new compounds with resonances at 143.5, 96.6, and 91.8 (intensities relative to **2** were 1.8, 0.56, and 0.16, respectively.) We presume the new materials to be stereoisomers of **2** (vide infra) and designate them **2a**, **2b**, and **2c** for the sake of discussion.[22] When the photolyzed sample was *rapidly* warmed to 32 °C, **2a–c** smoothly rearranged back to starting material **2** ($T_{1/2}$ = approximately 3 min at 32 °C) without producing phosphide **5**.[23]
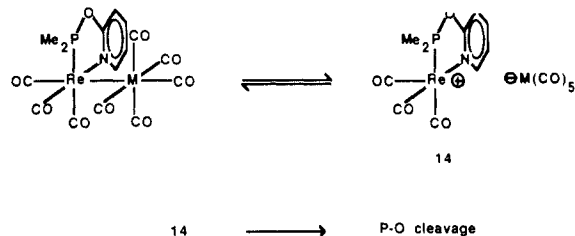
When **2** was photolyzed at 32 °C for 10 min, thermally quenched at −78 °C, and analyzed *immediately* at −84 °C, we observed **2**, **2a**, and **2c** (13:1:0.1), along with minor quantities of phosphide **5** and a new compound (−100.3 ppm). From the dramatically upfield shifted resonance, we presume that the P–O bond has been cleaved and designate the new compound as **5a**. When the photolyzed sample was allowed to stand at 23 °C, **2a**/**2c** and **5a** smoothly rearranged to **2** and **5**, respectively. (The $T_{1/2}$ for the conversion of **5a** to **5** was approximately 5 h.)

Chelate **2** was submitted to extended photolysis in toluene-d_8 at 32 °C. The sample was thermally quenched to −78 °C at 5-min intervals and monitored by low-temperature ^{31}P NMR spectroscopy. The ratio of **2**:**2a**:**2c** remained constant throughout the photolysis. The total concentration of **2**/**2a**/**2c** decreased as the concentrations of **5** and **5a** increased. As the photolysis proceeded, the concentration of **5a** increased relative to **5** to a maximum ratio
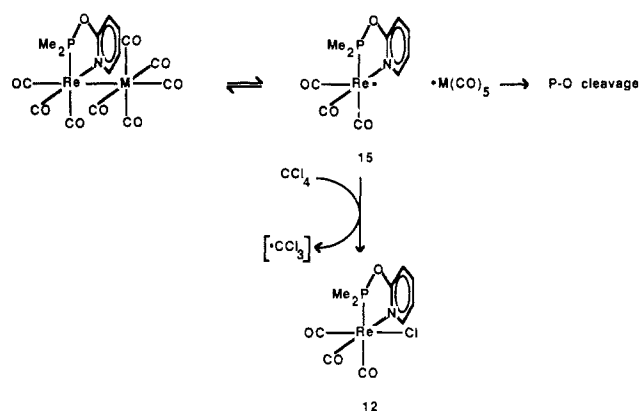
(18) Parshall, G. W. *Inorg. Synth.* **1974**, *15*, 191.

(19) Kawazoe, Y.; Yoshioka, Y. *Chem. Pharm. Bull.* **1968**, *16*, 715.

(20) In the normal EI mass spectra of **6**, significant dirhenium-containing peaks between 749 and 755 mass units made the crossover analysis impossible. Presumably, these arose from the formation of tetranuclear clusters during ionization.[21] Even in the field ionization mass spectra of **6**, traces of fragments in this region were observed (which were subsequently magnified by the 50-fold excess of **6** used in the crossover experiments). The 3:2 ratio of noncrossover:crossover may be a slight *under*estimate of the intramolecularity.

(21) Marcomini, A.; Pöe, A. *J. Am. Chem. Soc.* **1983**, *105*, 6952.

(22) For leading references to photochemical isomerizations of octahedral metal complexes, see: Ceulemans, A.; Beyens, D.; Vanquickenborne, L. G. *Inorg. Chem.* **1983**, *22*, 1113.

(23) Photolysis of **2** at −75 °C for 6.5 h afforded a complex mixture of compounds. Upon warming the sample to 25 °C, virtual quantitative conversion to starting material **2** occurred to the exclusion of P–O bond cleavage.

Scheme II

Scheme III

Scheme IV

of approximately 1.3:1. Further photolysis caused complete conversion of **2** to **5**.

The source of the photo-assisted P–O bond cleavage and a possible structure of **2a** are discussed in the next section.

Discussion

We considered four mechanisms for the rearrangements of chelates **2** and **3**. Since the thermal rearrangements exhibited first-order kinetics with no intermediates detected, we have focused on the first one or two primary steps that could initiate the P–O bond cleavages.

Mechanism I: Oxidative Addition. Transition metal-mediated bond cleavages are most often interpreted as an oxidative addition (net insertion) by a coordinatively unsaturated (16 electron) metal center. We have depicted in Scheme II one such pathway for the P–O cleavage involving CO dissociation. Since the rearrangements of **2** and **3** were not inhibited by 1 atm of CO, we would be forced to assume that the rate determining step was the CO dissociation (i.e., $k_{-1}[13][CO] \ll k_2[13]$). However, the significantly negative activation entropies measured for the rearrangement would argue against a rate determining dissociation of CO.[24] This would also require that the P–O cleavage step was at least a factor of 20 faster than the rate of CO return. Since the bimolecular rate constants for CO return to coordinatively unsaturated group 7, dinuclear carbonyl complexes are on the order of 10^4–10^5 M^{-1} s^{-1};[25] we feel that this would put an unrealistic lower limit on the rate of the P–O bond oxidative addition. In fact, the lack of inhibition by added CO seems to exclude *all* mechanisms that depend upon coordinatively unsaturated intermediates in the P–O cleavage step.

(24) Angelici, R. J. *Organomet. Chem. Rev.* **1968**, *3*, 173. Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557.

(25) Herrick, R. S.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 4550 and references cited therein.

Chart I

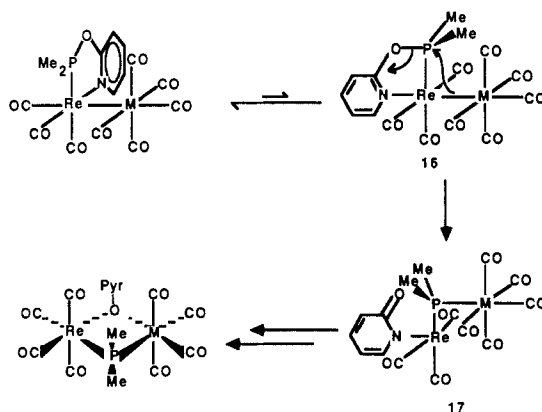Type I   Type II
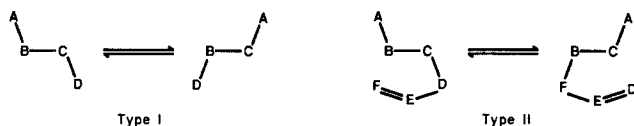
Scheme V

Mechanism II: Heterolytic Metal–Metal Bond Dissociation.
A mechanism for the rearrangements of **2** and **3** on the basis of a well documented[26] heterolytic metal–metal bond cleavage is depicted in Scheme III. The reaction is reminiscent of the ionic metal-mediated Arbuzov cleavages of P–C bonds.[27] Rate determining metal–metal bond heterolysis could be consistent with the measured negative $\Delta S^{\ddagger}$ values if the entropies of solvation were large enough to outweigh the positive entropic contributions of the fragmentation.[28] However, dramatic solvent effects on the observed reaction rates should have been observed regardless of which step was rate determining; the reaction rates were nearly independent of solvent. (As a crude comparison, we note that the rates of electrophilic cleavage of metal–metal bonds with I_2 were 10^5 faster in acetonitrile than toluene.[29]) We also failed to trap an intermediate metalate **14** with excesses of several methylating agents. Therefore, a mechanism involving metal–metal bond heterolytic cleavage is inconsistent with the data.

Mechanism III: Homolytic Metal–Metal Bond Dissociation.
We have depicted in Scheme IV the earliest stages of a mechanism for P–O bond cleavage involving metal–metal bond homolysis.

Several experiments implicated the *presence* of metal-centered radicals during the thermolyses of **2** and **3**. Using the well documented technique of scavenging metal radicals with CCl_4,[15] we observed a mixture of the normal P–O cleavage products along with metal chloride **12**. Poor reproducibility of the chlorination/P–O cleavage ratios was attributed to the hexachloroethane presumed to form during the course of the chlorination. The crossover studies uncovered nonstatistical intra- and intermolecular components to the rearrangements. Although the origins of the crossover products were not pinpointed, metal–metal bond homolysis is one possible source. Furthermore, the P–O cleavage was found to be photochemically accelerated at 32 °C. Since group 7 dinuclear complexes undergo photochemical metal–metal bond hydrolyses[30] this could be construed as evidence that metal radical **15** was an intermediate directly on the pathway to **5** and **6**.

However, we demonstrated that if the parent $M_2(CO)_{10}$ derivatives had been formed they would *not* have recycled into the reaction pathway. Therefore, we find it difficult to explain their absence in a reaction that appeared to generate the corresponding $M(CO)_5$ radicals. If we assume for the sake of discussion that metal-centered radicals were indeed formed during the course of the thermal rearrangements of **2** and **3**, there is still no direct evidence that such radicals were *on the P–O cleavage reaction pathway*. If a common radical intermediate **15** was partitioning between competing cleavage and chlorination pathways, the product ratio should have exhibited a dependence on the CCl_4 concentration.[31] Despite the poor quality of the chlorination data, the dependence of the product ratios on the concentration of the added CCl_4 was shown to be minimal. Furthermore, the observed partial crossover could have arisen if limited metal–metal bond homolysis occurred as a *side reaction*. Lastly, the photochemi-

cally-mediated cleavage of **2** did not necessarily arise from the production of high-energy radical intermediates. We will elaborate on this point in the presentation of mechanism IV.

Mechanism IV: Dyotropic Rearrangement. With mechanisms for the rearrangements of **2** and **3** involving the traditional reactive intermediates either excluded or rendered questionable, we sought an alternative mechanism involving a simple thermal isomerization. We provide the mechanism based on a dyotropic rearrangement (Scheme V) as one possibility.

Reetz defined a dyotropic rearrangement as the simultaneous intramolecular rearrangement (exchange) of two σ bonds and further defined two varieties as types I and II (Chart I).[32] Dyotropic rearrangements are typified by: (1) intramolecularity, (2) entropies of activation falling in the narrow range between −3 and −12 e.u., and (3) minimal dependencies of rates on solvent polarity. They appear to be most facile when the migrating fragments contain d orbitals (silicon or transition metals) or contain electronegative leaving groups and are often found in conjunction with competitive radical pathways.

The key P–O bond cleaving step (**16** to **17**) would represent a type II dyotropic rearrangement. The facility of the pyridyloxy group to function as a leaving group in displacements at phosphorus has been well documented.[4,5] Nevertheless, the rearrangement could occur with minimal charge buildup at any point along the reaction coordinate. (The reaction rates for the rearrangements of **2** and **3** showed minimal solvent dependencies.) Furthermore, the highly ordered transition state would be expected to exhibit the observed negative entropies of activation.

The stereochemical isomerization preceding the rate determining P–O bond cleavage requires some qualification. Of the four possible stereoisomers of chelate **2** (eight isomers of **3**), we invoke *mer* isomer **16** because it is the only isomer possessing the proper orbital alignments for the dyotropic rearrangement. Brown described a similar stereochemical isomerization on a dirhenium fragment that occurred at room temperature and was unaffected by added CO or CCl_4.[33] Seemingly related intramolecular stereochemical isomerizations of octahedral metal complexes are well-documented.[34,35] Since no intermediates in the rearrange-

(26) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528. Hieber, Von W.; Schropp, W., Jr. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1960**, *15*, 271. Mirbach, M. F.; Mirbach, M. B.; Wegman, R. W. *Organometallics* **1984**, *3*, 900.

(27) Brill, T. B. *Chem. Rev.* **1984**, *84*, 577.

(28) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1976; p 96.

(29) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 1308.

(30) Leading references: Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 3748. Leopold, D. G.; Vaida, V. *J. Am. Chem. Soc.* **1984**, *106*, 3720.

(31) In some instances, exceptionally rapid radical combination ($k = 10^{13}$–10^{14} s⁻¹) can compete with escape from the solvent cage and lead to zero-order dependence on the external radical scavenger, cf: Jacobsen, E. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 2023.

(32) Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33. For additional examples and leading references see: Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103. Collum, D. B.; Mohamadi, F.; Hallock, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6882.

(33) Nubel, P. D.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644.

(34) Pomeroy, R. K.; Hu, X. *Can. J. Chem.* **1982**, *60*, 1279. Vancia, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407. Darensbourg, D. J.; Gray, R. L. *Inorg. Chem.* **1984**, *23*, 2993. Pomeroy, R. K.; Vancea, L.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508. Fischer, H.; Fischer, E. O.; Werner, H. *J. Organomet. Chem.* **1974**, *73*, 331. Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680. Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14. Cotton, F. A.; Darensbourg, D. J.; Klein, S.; Kolthammer, B. W. S. *Inorg. Chem.* **1982**, *21*, 2661. Stewart, R. P. *Inorg. Chem.* **1979**, *18*, 2083. Dombek, B. D.; Angelici, R. *J. Am. Chem. Soc.* **1976**, *98*, 4110. Darensbourg, D. J.; Baldwin, B. *J. Am. Chem. Soc.* **1979**, *101*, 6447. Darensbourg, D. J.; Kudaroski, R.; Schenk, W. *Inorg. Chem.* **1982**, *21*, 2488. Alex, R. F.; Pomeroy, R. K. *J. Organomet. Chem.* **1985**, *284*, 379. Ismall, A. A.; Sauriol, F.; Sedman, J.; Butler, I. S. *Organometallics* **1985**, *4*, 1914.

2338 *J. Am. Chem. Soc., Vol. 108, No. 9, 1986*

Collum et al.

ments of either **2** or **3** were detected spectroscopically, the isomerization to **16** would have to be either rate determining or a spectroscopically invisible pre-equilibrium. Low-temperature photolyses of **2** effected clean isomerization to three new compounds that we presumed to be isomeric to **2** and simply designated them as **2a–c** (eq 2). Upon warming to 32 °C, **2a–c** isomerized quantitatively back to starting material **2** without affording any P–O bond cleavage product **5**. Although we do *not* know which one, if any, of the isomers correspond to mer isomer **16**, the spectroscopically invisible *pre-equilibrium* in Scheme V ($K_{eq} \ll$ 1) is quite plausible.

The apparent acceleration of the P–O cleavage by photolysis at ambient temperatures can be understood in the context of the pre-equilibrium in Scheme V. Photolysis of **2** at 32 °C maintained an elevated steady-state concentration of **2a/2b/2c** during the course of the photoaccelerated P–O cleavage.[22] A similar increased concentration of *mer* isomer **16** (irrespective of whether one of compounds **2a–c** corresponds to **16**) would proportionally increase the rate of the P–O cleavage step.

The photostationary conditions also appeared to alter the overall rate-determining step. Under the mild photochemical conditions, we observed a second intermediate resonance at –100.3 ppm consistent with a structure containing a cleaved P–O bond (designated **5a**; eq 2). Upon standing at 32 °C, this intermediate disappeared with concomitant increase in the resonance corresponding to **5**.

Summary and Conclusions

The rearrangements of **2** and **3** involve facile cleavage of an 80+ kcal/mol phosphorus–oxygen bond.[3] We excluded mechanisms based on oxidative additions to coordinatively unsaturated intermediates or metal–metal bond heterolyses. Metal-centered radicals may have been generated during the course of the reaction, but their direct involvement in the P–O bond cleavage is questionable. During the course of our studies on metal–metal homolytic bond cleavages, we found that C_2Cl_6 *rapidly* chlorinated dinuclear complexes **2** and **3** by a mechanism that did *not* appear to involve radical scavenging in a post-rate-determining step. Since C_2Cl_6 is a likely by-product from chlorinations of metal radicals by CCl_4, using CCl_4 as an innocent radical scavenger must be done with caution.

With the more traditional bond scission mechanisms in question, an alternative mechanism for the P–O bond cleavage based on a dyotropic rearrangement was presented. The dyotropic rearrangement exhibited three intriguing qualities. The critical P–O bond cleaving step (**16** to **17**) formally represents a direct oxidative addition across two different metal centers.[37] Furthermore, in sharp contrast with normal bond cleavages that proceed by oxidative additions, the dyotropic rearrangement mechanism involves a cleavage by a coordinatively *saturated* "reactive intermediate" **16** to produce a coordinatively *unsaturated* product **17**. Lastly, the proposed mechanism for photochemical activation involved neither a 17 electron radical (bond homolysis) nor a 16 electron

(35) The failure of added CO to inhibit the rearrangements of **2** and **3** does not necessarily exclude a CO dissociation mechanism for the stereochemical isomerization to the mer isomers. If the rate of stereochemical equilibration in a pentacoordinate intermediate is faster than CO return, the rate of isomerization (and, in turn, the rate of the P–O cleavage), would be independent of CO concentration.

(36) A referee suggested that treatment of $Re_2(CO)_8(\mu\text{-H})(\mu\text{-CH}=CHBu)$ might afford an alternative stereoisomer [e.g., $Re_2(CO)_8(\mu\text{-1})$] according to the method of Brown.[33] We had carried out this reaction and observed the kinetic formation of *at least* eight different compounds by ^{31}P NMR spectroscopy [including a bis(phosphine) adduct exhibiting an AB quartet]. Upon standing at room temperature for 5 days, a host of exchanges could be observed whereupon all of the resonances eventually converged to one resonance at –68.1 ppm corresponding to P–O cleavage product **5** (54% isolated yield). The experiment was intriguing, yet far too complex for a detailed interpretation.

(37) *Direct* oxidative addition across a metal–metal σ bond has not been rigorously documented and appears to be energetically unfavorable for a four-centered mechanism. Leading references: Halpern J. *Inorg. Chim. Acta* **1982**, *62*, 31. Sevin, A.; Hengtai, Y.; Chaquin, P. *J. Organomet. Chem.* **1984**, *262*, 391.

intermediate (ligand dissociation) per se. The photoactivation was proposed to arise from a photostationary state that increased the effective concentration of the reactive stereoisomer.

Experimental Section

Kinetics. The kinetics were monitored by ^{1}H NMR spectroscopy on the Bruker WM-300 spectometer. In a typical run, 10.0 mg of dinuclear **2** (or **3**) was dissolved in 0.50 mL of fully dried and degassed toluene-d_8 in a 5-mm NMR tube that was then sealed under vacuum. The tube was heated in a constant temperature bath (±0.1 °C) and removed at appropriate intervals to record the spectra. Loss of starting material was followed by integration of the peak at 8.20 ppm (relative to the solvent peak). The first-order rate constants were determined by a least-squares fit to a plot of $\ln([2]/[2]_0)$ vs. time (t). Measurements of the rate over a 52 °C temperature range afforded ΔH^* and ΔS^* values from a nonlinear, weighted least-squares fit of a plot of k vs. T. The corresponding linear least-squares fits gave the same results within experimental error.

fac-$L_2Re(CO)_3Br$ (**4**, L_2 = 2-Pyridyl Dimethylphosphinite). A solution of $BrRe(CO)_5$ (3.91 g, 9.63 mmol) in toluene (60 mL) under argon at 60 °C was treated with ligand **1** (1.55 g, 10.0 mmol) and then heated to 120 °C for an additional 15 min. The solution was cooled to room temperature and filtered free of solid material. Partial removal of solvent in vacuo (until precipitation began) and addition of an equal volume of hexane and then filtration afforded 4.23 g (88% yield) of **4** as a white solid: mp 133–135 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 8.10 (dd, $J_{H–H}$ = 1.75, 5.9 Hz, 1 H), 6.55 (m, 1 H), 6.21 (d, $J_{H–H}$ = 8.4 Hz, 1 H), 5.77 (m, 1 H), 1.67 (d, $J_{P–H}$ = 7.5 Hz, 3 H), 1.28 (d, $J_{P–H}$ = 6.6 Hz, 3 H); ^{31}P{^{1}H} NMR (C_6D_6) δ 145.5 (s); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 193.1 (d, $J_{P–C}$ = 6.3 Hz), 192.6 (d, $J_{P–C}$ = 76.2 Hz), 188.9 (d, $J_{P–C}$ = 7.9 Hz), 164.2 (d, $J_{P–C}$ = 3.2 Hz), 152.9 (d, $J_{P–C}$ = 4.8 Hz), 142.4 (s), 120.2 (s), 112.6 (d, $J_{P–C}$ = 4.8 Hz), 22.3 (d, $J_{P–C}$ = 31.7 Hz), 17.0 (d, $J_{P–C}$ = 30.2 Hz); IR (C_6D_6) (CO) 2020 (s), 1950 (s), 1905 (s) cm⁻¹. Anal. Calcd for $C_{10}H_{10}ReBrO_4P$: C, 23.77; H, 1.99; N, 2.77. Found: C, 23.72; H, 2.14; N, 2.79.

fac-$L_2Re(CO)_3[Re(CO)_5]$ (**2**, L_2 = 2-Pyridyl Dimethylphosphinite). A solution of $Re(CO)_5Na$ was prepared by stirring $Re_2(CO)_{10}$ (0.805 g, 1.24 mmol) and 2% Na/Hg (5.7 g, 4.96 mmol of Na) in 10 mL of THF at 25 °C for 1.5 h. The solution containing the anion was drawn up into a gas-tight syringe and added to a suspension of **4** (0.50 g, 0.99 mmol) in THF (15 mL) under argon at –78 °C. The reaction was held at –78 °C for 2 h and at 25 °C for an additional 12 h. The solvent was removed in vacuo, and the gummy residue was extracted with 2 × 50 mL of toluene. Partial concentration of the combined toluene extracts followed by layering with hexane caused precipitation of a yellow solid. Filtration and drying in vacuo afforded 362 mg (49% yield) of **2**: mp 140–142 °C dec; ^{1}H NMR (300 MHz, C_6D_6) δ 8.24 (dd, $J_{H–H}$ = 1.6, 5.8 Hz, 1 H), 6.45 (m, 1 H), 6.26 (d, $J_{H–H}$ = 8.2 Hz, 1 H), 5.74 (m, 1 H), 1.61 (d, $J_{P–H}$ = 6.5 Hz, 3 H), 1.54 (d, $J_{P–H}$ = 6.2 Hz, 3 H), ^{31}P{^{1}H} NMR (C_6D_6) δ 139.6 (s); ^{31}P{^{1}H} NMR (toluene-d_8) δ 140.5 (s); ^{13}C{^{1}H} NMR (C_6D_6) δ 202.8 (s), 199.8 (m), 191.0 (s), 163.4 (d, $J_{P–C}$ = 4.8 Hz), 152.3 (d, $J_{P–C}$ = 4.8 Hz), 140.1 (s), 119.0 (s), 111.8 (d, $J_{P–C}$ = 6.4 Hz), 26.5 (d, $J_{P–C}$ = 31.7 Hz), 25.0 (d, $J_{P–C}$ = 27.0 Hz); IR (C_6D_6) (CO) 2080 (m), 2050 (sh), 2010 (s), 1970 (s), 1950 (m), 1900 (s) cm⁻¹. Anal. Calcd for $C_{15}H_{10}Re_2NO_9P$: C, 23.97; H, 1.33; N, 1.86; P, 4.12. Found: C, 24.03; H, 1.50; N, 2.01; P, 4.00.

fac-$L_2Re(CO)_3[M(CO)_5]$ (**3**, L_2 = 2-Pyridyl Dimethylphosphinite). A solution of $Mn(CO)_5Na$ was generated by stirring $Mn_2(CO)_{10}$ (1.00 g, 2.56 mmol) and 2% Na/Hg (11.4 g, 9.90 mmol of Na) in THF (15 mL) at 25 °C for 2 h. The solution of the anion was drawn up by gas-tight syringe and added to a suspension of **4** (1.00 g, 1.98 mmol) in THF (10 mL) at –78 °C. The reaction vessel was allowed to warm, and the contents were stirred at 25 °C for 20 h. Following removal of the solvent in vacuo and extraction of the resulting gummy oil with 3 × 30 mL of benzene, the combined extracts were partially concentrated and layered with hexane. The resulting precipitate was filtered and dried in vacuo to afford **3** (540 mg, 44% yield) as a pale yellow solid: mp 118–120 °C dec; ^{1}H NMR (300 MHz, C_6D_6) δ 8.24 (dd, $J_{H–H}$ = 1.1, 5.8 Hz, 1 H), 6.50 (m, 1 H), 6.28 (d, $J_{H–H}$ = 8.3 Hz, 1 H), 5.78 (m, 1 H), 1.59 (d, $J_{P–H}$

= 6.6 Hz, 3 H), 1.51 (d, J_{P-H} = 6.3 Hz, 3 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 143.0 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 226.0 (br), 202.3 (d, J_{P-C} = 71.3 Hz), 197.9 (d, J_{P-C} = 6.4 Hz), 187.8 (d, J_{P-C} = 9.5 Hz), 163.6 (d, J_{P-C} = 3.2 Hz), 152.2 (d, J_{P-C} = 4.8 Hz), 140.9 (s), 119.3 (s), 112.1 (d, J_{P-C} = 6.4 Hz), 25.8 (d, J_{P-C} = 33.3 Hz), 22.8 (d, J_{P-C} = 27.0 Hz); IR (C_6D_6) (CO) 2070 (m), 2010 (s), 1965 (s), 1940 (s), 1910 (m) cm^{-1}. Anal. Calcd for $C_{15}H_{10}MnReNO_9P$: C, 29.04; H, 1.61; N, 2.26; P, 5.00. Found: C, 29.20; H, 1.61; N, 2.29; P, 4.90.

(CO)₄Re(μ-OPYR)(μ-PMe₂)Re(CO)₄ (5). A solution of dinuclear **2** (47 mg, 0.062 mmol) in toluene (10 mL) was heated to 70 °C in an evacuated glass bomb reactor for 18 h. Removal of the solvent in vacuo followed by flash chromatography (7.5% ether/hexane) afforded phosphide **5** (44 mg, 94% yield) as a colorless solid: mp 88–90 °C; ^1H NMR (300 MHz, C_6D_6) δ 7.65 (m, 1 H), 6.77 (m, 1 H), 6.59 (d, J_{HH} = 8.4 Hz, 1 H); 5.65 (m, 1 H), 1.93 (d, J_{PH} = 6.9 Hz, 6 H); ^1H NMR (90 MHz, CD_2Cl_2, 28 °C) δ 7.67 (m, 1 H), 7.21 (m, 1 H), 6.62 (m, 1 H), 6.25 (m, 1 H), 2.25 (d, J_{PH} = 6.8 Hz, 6 H); ^1H NMR (90 MHz, CD_2Cl_2, -80 °C); ^1H NMR (90 MHz, CD_2Cl_2, -74 °C) the six proton doublet corresponding to the $P(CH_3)_2$ moiety at 2.25 ppm appears as two doublets at δ 2.30 (d, J_{PH} = 4.89 Hz, 3 H) and δ 2.06 (d, J_{PH} = 5.86 Hz, 3 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ -68.1 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 190.4 (m), 178.9 (s), 153.1 (s), 141.2 (s), 116.6 (s), 114.3 (s), 20.4 (d, J_{PC} = 22.2 Hz); IR (C_6D_6) (CO) 2085 (m), 2005 (s), 1990 (s), 1940 (s), 1930 (s) cm^{-1}. Anal. Calcd for $C_{15}H_{10}NO_9PRe_2$: C, 23.97; H, 1.33, N, 1.86; P, 4.12. Found: C, 24.04; H, 1.44; N, 1.75; P, 4.25.

(CO)₄Re(μ-OPYR)(μ-PMe₂)Mn(CO)₄ (6). A solution of chelate **3** (0.203 g, 0.33 mmol) in toluene (10 mL) was heated to 70 °C in an evacuated glass tube for 18 h. Removal of the solvent in vacuo followed by flash chromatography (5% diethyl ether/hexane) afforded phosphide **6** (192 mg, 95% yield) as a pale yellow solid: mp 73–74 °C; ^1H NMR (300 MHz, C_6D_6) δ. 7.68 (m, 1 H), 6.80 (m, 1 H), 6.62 (d, J_{HH} = 8.3 Hz, 1 H), 5.69 (m, 1 H), 1.84 (d, J_{PH} = 6.8 Hz, 6 H); ^1H NMR (90 MHz, CD_2Cl_2, 28 °C) δ 8.16 (m, 1 H), 7.40 (m, 1 H), 6.84 (m, 1 H), 6.43 (m, 1 H), 1.99 (d, J_{PH} = 6.8 Hz, 6 H); ^1H NMR (90 MHz, CD_2Cl_2, -74 °C) the six proton doublet corresponding to the $P(CH_3)_2$ moiety at 1.99 ppm appears as two doublets at δ 2.10 (d, J_{PH} = 6.3 Hz, 3 H) and δ 1.96 (d, J_{PH} = 6.1 Hz, 3 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ -20.5 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 212.10 (br), 190.34 (m), 153.07 (s), 140.82 (s), 118.07 (s), 113.42 (s), 20.41 (d, J_{PC} = 17.5 Hz); IR (C_6D_6) (CO) 2075 (m), 2000 (s), 1990 (s), 1945 (s). Anal. Calcd for $C_{15}H_{10}MnNO_9PRe$: C, 29.04; H, 1.61; N, 2.26; P, 5.00. Found: C, 29.19; H, 1.71; N, 2.28; P, 4.97.

fac-L₂Mn(CO)₃Br (9, L₂ = 2-Pyridyl Dimethylphosphinite). A solution of $BrMn(CO)_5$ (2.0 g, 7.28 mmol) in toluene (30 mL) at 60 °C was treated with **1** (1.55 g, 10.0 mmol) and the further warmed to 120 °C for 15 min. Cooling to 25 °C, filtering, concentrating the filtrate to approximately 20 mL, and vacuum transferring in 20 mL of hexane effected precipitation of **9** as a yellow orange solid. Filtering and drying in vacuo afforded 1.92 g (71% yield): ^1H NMR (300 mHz, C_6D_6) δ 8.15 (m, 1 H), 6.61 (m, 1 H), 6.23 (m, 1 H), 5.95 (m, 1 H), 1.87 (d, J_{PH} = 7.4 Hz, 3 H), 1.32 (d, J_{PH} = 5.7 Hz, 3 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 195.9 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 220.9–213.1 (br m), 163.4 (d, J_{PC} = 4.8 Hz), 152.4 (d, J_{PC} = 4.8 Hz), 141.4 (s), 119.5 (s), 112.0 (d, J_{PC} = 4.8 Hz), 21.3 (d, J_{PC} = 25.4 Hz), 17.9 (d, J_{PC} = 25.4 Hz); IR (C_6D_6) (CO) 2025 (s), 1960 (s), 1910 (s) cm^{-1}. Anal. Calcd for $C_{10}H_{10}BrMnNO_4P$: C, 32.11; H, 2.70; N, 3.75. Found: C, 31.98; H, 2.75; N, 3.62.

(CO)₄Mn(μ-OPYR)(μ-PMe₂)Mn(CO)₄ (10). A solution of $NaMn(CO)_5$ was prepared by stirring $Mn_2(CO)_{10}$ (0.89 g, 2.28 mmol) and 2% Na/Hg (10.5 g, 9.12 gm atoms of Na) in THF (15 mL) at 25 °C for 1.25 h. The solution of anion was drawn into a gas-tight syringe and added to a solution of **9** (0.75 g, 0.20 mmol) in THF (10 mL) under argon at -78 °C. The mixture was stirred at -78 °C for 0.5 h and at 25 °C for an additional 17 h. The solvent was removed in vacuo, and the residue was extracted with 2 × 20 mL of toluene. The toluene extracts were concentrated to 20 mL and heated to 75 °C for 20 h. Removal of the toluene in vacuo and flash chromatography of the residue (10% diethyl ether/hexane) afforded 340 mg (30% yield) of **10** as a red-orange oil. When the crude mixture was examined by ^{31}P NMR (C_6D_6) prior to thermolysis, peaks at 235.1, 196.7, 195.9, and 113.5 ppm were evident. Heating caused the resonance at 196.7 ppm to be replaced by a resonance at 28.7 corresponding to phosphide **10**. The resonance at 113.5 ppm seemed to be replaced by a resonance at 125.5. Phosphide **10**: ^1H NMR (80 MHz, C_6D_6) δ 7.50 (m, 1 H), 6.75 (br m, 1 H), 6.50 (br m, 1 H), 5.75 (br m, 1 H), 1.70 (d, J_{PH} = 6.6 Hz, 6 H); ^1H NMR (90 MHz, CD_2Cl_2, 28 °C) δ 7.98 (br m, 1 H), 7.46 (br m, 1 H), 6.73 (br m, 1 H), 6.49 (br m, 1 H), 1.99 (d, J_{PH} = 6.8 Hz, 6 H); ^1H NMR (90 MHz, CD_2Cl_i, -80 °C) the six proton doublet of the PMe_2 moiety appears as two broad singlets at 2.08 and 1.80 ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 28.7 (s); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 218.4–212.0 (br), 181.0 (s), 152.4 (s), 140.0 (s), 118.7 (s), 112.9 (s), 20.4 (d, J_{PC} = 12.7 Hz); IR (C_6D_6) (CO)

2060 (m), 2000 (s), 1990 (s), 1950 (m) cm^{-1}. Satisfactory analysis was not obtained.

(CO)₄Re(μ-OPYR)(μ-PMe₂)Mn(CO)₄ (6) was obtained from Bromide **9**. A solution of $NaRe(CO)_5$ was prepared by stirring $Re_2(CO)_{10}$ (1.10 g, 1.70 mmol) and 2% Na/Hg (7.82 g, 6.8 mmol of Na) in THF (10 mL) at 25 °C for 1.5 h. The solution of the anion was drawn into a gas-tight syringe and added to a solution of **9** (0.853 g, 2.28 mmol) in THF (10 mL) under argon at -78 °C. The reaction was stirred at -78 °C for 1.0 h and at 25 °C for an additional 21 h. The solvent was removed in vacuo, and the residue was extracted with benzene (2 × 15 mL). Concentration of the benzene extracts and analysis by ^{31}P (C_6D_6) showed resonances corresponding to starting material **9** and phosphide **6** as well as resonances at 98.9, 113.6, and 236.3 ppm. If the mixture was heated at 70 °C for 24 h and monitored, the peak at 197.1 ppm disappeared with concomitant increase of the resonance at -20.5 ppm corresponding to phosphide **6**. Workup as described above afforded 381 mg of pure **6** (27% yield).

Trapping Experiment: Triphenylphosphine. A 5-mm NMR tube was charged with a solution of **2** (0.013 mmol), 0.5 mL of C_6D_6, and triphenylphosphine (17 mg, 0.065 mmol). The tube was removed from the glovebox, sealed under vacuum, and heated at 80 °C with monitoring by ^{31}P NMR. The rearrangement occurred without appearance of intermediate resonances. Upon extended heating, a series of phosphine substitution products appeared that converged to an approximately 90% pure compound exhibiting an AB quartet. The new compound was isolated and purified as follows. A solution of **2** (0.156 g, 0.21 mmol) and PPh_3 (0.055 g, 0.21 mmol) in toluene (5.0 mL) was heated at 85 °C in a sealed, evacuated glass tube for 35 h. Concentration of the solution in vacuo followed by flash chromatography (5% ether in hexane) and recrystallization from ether/hexane afforded 71 mg of **11** (38% yield) as a yellow solid (approximately 90% pure): ^1H NMR (300 mHz, C_6D_6) δ 7.83 (dd, J_{HH} = 1.9 and 6.1 Hz, 1 H), 7.71 (m, 6 H), 7.13 (m, 9 H), 6.76 (m, 1 H), 5.66 (m, 1 H), 5.42 (d, J_{HH} = 8.4 Hz, 1 H), 2.29 (dd, J_{PH} = 1.2 and 7.03 Hz, 6 H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 14.81 (d, J_{PP} = 117.2 Hz), -68.11 (d, J_{PP} = 117.2 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 197.0 (m), 192.2–186.5 (br m), 177.3 (s), 153.2 (s), 139.9 (s), 134.7 (d, J_{PC} = 42.8 Hz), 134.1 (d, J_{PC} = 11.1 Hz), 130.3 (s), 128.5 (s), 117.7 (s), 113.5 (s), 21.9 (d, J_{PC} = 22.2 Hz); IR (C_6D_6) (CO) 2090 (w), 1995 (s), 1980 (s), 1940 (s), 1885 (m) cm^{-1}.

Trapping: MeI. A 5-mm NMR tube was charged with a solution of 10 mg of **2**, 0.40 mL of C_6D_6, and methyl iodide (150 mg, 1.06 mmol). The tube was removed from the glovebox, sealed under vacuum, and heated at 80 °C for 20 h. To avoid problems in the NMR analysis due to the gross excess of methyl iodide, the NMR tube was broken open in the glovebox, and the volatile was removed in vacuo. The 300-MHz ^1H NMR spectrum of the nonvolatile residue showed only **5** to the exclusion of the resonance at -0.20 ppm corresponding to an authentic samples of $MeRe(CO)_5$. A similar experiment using dinuclear **3** afforded **6** to the exclusion of $MeMn(CO)_5$.

Trapping: CCl₄. In a typical experiment, 10.0 mg of **2** (or **3**) were dissolved in C_6D_6 in a 5-mm NMR tube. The appropriate amount of CCl_4 was then added. The total volume was kept at 0.50 mL. The tube was transferred from the glovebox and sealed under vacuum. The tube was immersed in an 80.0 °C thermostated bath for 12 h (or 2.0 h for **3**) with complete exclusion of room light. The chlorination/P–O cleavage ratios were measured by integrating the PMe_2 methyl resonances of chloride **12** and phosphide **5** (or **6**) in the 300-MHz ^1H NMR spectrum. Chloride **12**: ^1H NMR (300 MHz, C_6D_6/CCl_4) δ 8.12 (m, 1 H), 6.62 (m, 1 H), 6.27 (m, 1 H), 5.86 (m, 1 H), 1.58 (d, J_{PH} = 7.5 Hz, 3 H), 1.33 (d, J_{PH} = 6.5 Hz, 3 H); $^{31}P\{^1H\}$ NMR (C_6D_6/CCl_4) δ 151.0.

Crossover Experiment: Method A. A solution of **2** (10.0 mg, 0.013 mmol) and $Mn_2(CO)_{10}$ (26 mg, 0.067 mmol) in 0.40 mL of C_6D_6 in a sealed NMR tube under vacuum was heated to 85 °C for 22 h. The 300-MHz ^1H NMR spectrum showed dirhenium phosphide **5** to the exclusion of heteronuclear phosphide **6**. A similar experiment involving heating heteronuclear chelate **3** in the presence of $Re_2(CO)_{10}$ afforded heteronuclear phosphide **6** to the exclusion of **5**.

Crossover Experiment: Method B. A mixture of **2-d_2** (5 mg, 0.0066 mmol) and **3-d_0** (206 mg, 0.332 mmol) was dissolved in 2.0 mL of C_6D_6 and placed in an NMR tube that was then sealed under vacuum. After heating at 80 °C for 40 h, the tube was broken open, the solvent was removed in vacuo, and the residue was flash chromatographed on silica gel with 10% diethyl ether in hexane as eluant (**5** and **6** were inseparable even on an analytical HPLC). The mixture was analyzed by using field ionization mass spectrometry at the University of Illinois mass spectrometry facility. Quantitative integration of the peaks at 751, 753, and 755 m/e corresponding to **5-d_2**, superimposed upon by peaks at 749, 751, and 753 corresponding to **5-d_0**, showed that the rearrangement had occurred to give an approximate 3:2 mixture of **5-d_2:5-d_0** (noncrossover: crossover). The complementary experiment using **2-d_0** and a 50-fold

excess of 3-d_2 afforded an analogous 3:2 mixture of 5-d_0:5-d_2. Despite complications by trace dirhenium containing impurities in this region of the spectrum that arose from the heteronuclear fragment 6,[23] it was clear that the crossover components were significant. Furthermore, because of the statistical bias imparted by the 50-fold excess, the noncrossover components were significant.

Photolyses of Chelate 2. A solution of 2 (30 mg) in toluene-d_8 (0.40 mL) was placed in a 5-mm NMR tube along with a capillary containing a PCl_3 internal ^{31}P NMR standard. The tube was sealed under vacuum, placed in a thermostatically controlled acetone bath, and photolyzed with a 250-W sunlamp. The photolyses at 32 °C were thermally quenched at −78 °C to prevent thermal isomerizations back to starting material 2. The ^{31}P NMR spectra were recorded without letting the sample warm above −78 °C. Further details of the experiments are described in the Results section.

Temperature Dependence of the Homolytic Abstraction of Benzylic Hydrogen by Bromine Atom

J. G. Wright and R. D. Gilliom*

Contribution from the Department of Chemistry, Rhodes College, Memphis, Tennessee 38112. Received August 5, 1985

Abstract: The abstraction of benzylic hydrogen by bromine atom from toluene and 4-chlorotoluene has been studied by measuring the relative rates at 45.0, 25.0 10.0, 0.0, −18.5, −32.0, and −50.0 °C. The rates of 3-chloro-, 4-bromo-, 4-methyl-, and 4-nitrotoluenes relative to toluene were determined at −50.0 °C. A peculiar Arrhenius plot, a change in the sign of the slope, was observed. A Hammett plot with a ρ value of −0.376 was obtained at the low temperature with the better fit with σ. The results are discussed in terms of the generally accepted interpretation of the polar effect.

The most common reaction of free radicals is the abstraction of hydrogen.[1] When toluenes serve as the hydrogen donors in this reaction, a Hammett correlation is observed.[1] While some radicals give better regressions with σ and others with σ^+, the interpretation of the "polar effect", as generally accepted, was given by Russell.[2] The Hammett correlations of a number of abstracting radicals have been summarized.[3] This explanation of the polar effect rests upon the idea of stabilization of the transition-state structure by a polar canonical structure, II. This

$$ArCH_3 + X \rightarrow [ArCH_2H \ X \leftrightarrow ArCH_2 \ H{:}X] \rightarrow$$
$$\qquad\qquad\qquad\quad I \qquad\qquad\quad II$$

$$ArCH_2 + HX$$
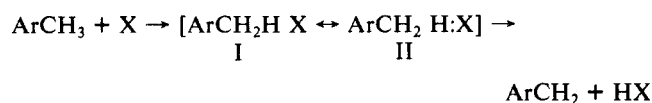
interpretation was based upon the observation that most abstracting radicals correlate with a negative value for ρ in Hammett-type plots; i.e., electron-withdrawing substituents slow the reaction.[3] This polar interpretation of substituent effects seemed strengthened by the discovery that radicals of low electronegativity, *tert*-butyl,[4] 3-heptyl,[5] and undecyl[6] afforded Hammett correlations with a positive ρ value.

Zavitsas and Pinto[7] proposed that charge separation in the transition state either does not occur or is an unnecessary assumption. These workers argued that the differences in reactivities of a series of substituted toluenes toward a radical were due to differences in the bond dissociation energies, BDE, of the benzylic C–H bonds in each of the substrates. This argument depends upon the assumption that electron-withdrawing substituents increase the BDE and was based upon the observation of only negative values of ρ for several abstracting radicals. This proposition was questioned by the finding of positive values of ρ for abstraction reactions.[4-6] The Pryor group concluded that both the polar effect upon the transition state and upon bond dissociation energies must be considered.[8]

More recently, Dust and Arnold have presented a σ· scale based upon benzylic α-hydrogen electron-spin resonance hyperfine coupling constants.[9] This work reexamined a series of radical reactions using an extended Hammett relation to attempt to assess the relative importance of spin delocalization (radical stabilization) vs. polar effects in radical reactions. They concluded that polar effects were dominant in the bromine atom abstraction of hydrogen from substituted toluenes. Recently it was reported[10] that this reaction has a "two-point" isokinetic temperature[10,11] of 276 K in benzene solution, a result consistent with an entropic, not an enthalpic, interpretation.

It is interesting to note that only one study has examined the role of temperature upon the homolytic polar effect as revealed by using linear free-energy relationships.[12] These workers reported that bromination using *N*-bromosuccinimide was best fit when using σ^+ from 10 to 80 °C. Their results may be extrapolated to give an isokinetic temperature of about −80 °C, and they reported that 4-chlorotoluene did not fit their otherwise "excellent" isokinetic relationship.

(1) Pryor, Wm. A. *Free Radicals*; McGraw-Hill: New York, 1966.
(2) Russell, G. A. *J. Org. Chem.* **1958**, *23*, 1407.
(3) Pryor, Wm. A.; Lin, T. H.; Stanley, J. P.; Henderson, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 6993.
(4) (a) Pryor, Wm. A.; Davis, Wm. H.; Stanley, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 4754. (b) Ptyor, Wm. A.; Church, D. F.; Tang, F. Y.; Tang, R. H. *Frontiers of Free Radical Chemistry*; Academic: New York, 1980; pp 355–379. (c) Pryor, Wm. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885.
(5) Henderson, R. W. *J. Am. Chem. Soc.* **1975**, *97*, 213.
(6) Pryor, Wm. A.; Davis, Wm. H. *J. Am. Chem. Soc.* **1974**, *96*, 7556.
(7) Zavitsas, A. A.; Pinto, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 7390.

(8) Davis, Wm. H.; Gleaton, J. H.; Pryor, Wm. A. *J. Org. Chem.* **1977**, *42*, 7. Davis, Wm. H.; Pryor, Wm. A. *J. Am. Chem. Soc.* **1977**, *99*, 6365.
(9) Dust, J. M.; Arnold, D. R. *J. Am Chem. Soc.* **1983**, *83*, 6531.
(10) Gilliom, R. D.; Brewer, R. M.; Miller, K. R. *J. Org. Chem.* **1983**, *48*, 3600.
(11) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactons*; Wiley: New York, 1963; Chapter 9.
(12) Kim, S. S.; Kang, C. H.; Choi, S. Y. *Abstr. Pap.—Am. Chem. Soc.* **1984**, *187*, ORGN 171; *J. Am. Chem. Soc.* **1985**, *107*, 4234.