Contribution from the J. Tuzo Wilson Laboratories, Erindale College,
University of Toronto, Mississauga, Ontario, Canada L5L 1C6

Substituent Effects on the Strengths of Some Manganese–Manganese Bonds

RONALD A. JACKSON and ANTHONY POË*

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Kinetic studies have been made of the thermal decomposition (in decalin and under an atomosphere of oxygen) of the axially substituted complexes $Mn_2(CO)_8L_2$ [L = $PPhEt_2$, PPh_2Et, $PPh(OMe)_2$, $PPh_2(OMe)$, or $P(p\text{-}MeOC_6H_4)_3$]. The activation enthalpies for these $[O_2]$-independent reactions are assigned to homolytic fission of the Mn–Mn bonds and are found to fall on or near a smooth plot of $\Delta H^{\ddagger}_{\mathrm{hf}}$ against cone angle of L. A more detailed analysis of the steric contribution to the values of $\Delta H^{\ddagger}_{\mathrm{hf}}$ shows that they do not interpolate linearly between the values for the "unmixed" ligands $P(OMe)_3$ or PEt_3 and PPh_3, and suggestions are made to account for this. The analysis also allows a value of 127 ± 8° to be assigned to the cone angle of triphenylarsine.

The establishment of homolytic fission as the initial slow step in several reactions of $M_2(CO)_{10}$ (M_2 = Mn_2, MnRe, Tc_2, or Re_2)[1] and some axially substituted derivatives[2] opened the way to quantitative kinetic measurement of the strengths of the metal–metal bonds and an investigation of the effects of various substituents on these strengths.[3] We have shown[3] that there are relatively small but significant electronic effects governing the bond strengths but that the main factor determining the strength of Mn–Mn bonds is the size and number of the axial substituents. The steric effect manifests itself in a release of steric strain as the Mn–Mn bond stretches. We report here a study of the effects of several other substituents that confirms our earlier conclusion and shows that certain subtleties in the operation of the steric effect can also be detected in this way.

The reaction chosen to provide these data was decomposition under oxygen, a reagent that effectively scavenges the mononuclear radicals when they are produced by the homolytic fission process.[1,2]

Experimental Section

The ligands ethyldiphenylphosphine,[4] diethylphenylphosphine,[5] and tris(*p*-methoxyphenyl)phosphine[5] were prepared according to published procedures. $P(p\text{-}MeOC_6H_4)_3$ was recrystallized from methanol, and $PEtPh_2$ and PEt_2Ph were distilled before use under reduced pressure (3 mmHg) at 112–113 and 58–59 °C, respectively. The axially substituted complexes $Mn_2(CO)_8L_2$ (L = $PEtPh_2$, PEt_2Ph, and $P(p\text{-}MeOC_6H_4)_3$) were prepared by photochemical reaction of $Mn_2(CO)_{10}$ with a fivefold excess of ligand according to the method of Osborne and Stiddard.[6] Solutions were thoroughly degassed and contained in Schlenk tubes under slightly reduced pressure (400 mmHg) before irradiation to avoid buildup of unnecessarily high pressures due to the release of CO during the reaction. Irradiation was effected simply in sunlight for 30–50 h and yields were from 40 to 90%. The purity of the samples was checked spectroscopically.[6b] The complexes $Mn_2(CO)_8\{PPh(OMe)_2\}_2$ and $Mn_2(CO)_8\{PPh_2(OMe)\}_2$ were a gift from Dr. E. Singleton of the National Chemical Research Laboratory, Pretoria, South Africa. Strong IR bands were shown in decalin at 1952 (L = $PPhEt_2$), 1958 (L = PPh_2Et), 1955 (L = $P(p\text{-}MeOC_6H_4)_3$), 1965 (L = $PPh(OMe)_2$), and 1963 cm^{-1} (L = $PPh_2(OMe)$) which compare as expected with strong bands at 1967 (L = $P(OMe)_3$), 1950 (L = PEt_3), and 1960 cm^{-1} (L = PPh_3) and with other spectroscopic data (e.g., ref 6b).

With the exception of $Mn_2(CO)_8\{P(p\text{-}MeOC_6H_4)_3\}_2$ the complexes were dissolved in decalin and kinetic runs for reaction with oxygen were performed exactly as described before.[1,2] The complex $Mn_2(CO)_8\{P(p\text{-}MeOC_6H_4)_3\}_2$ was difficult to dissolve in decalin. Solutions for kinetic study were prepared by dissolving the sample in a few drops of dichloromethane and diluting the solution with enough decalin to provide the desired concentration of complex. The CH_2Cl_2 was then removed under reduced pressure. Solutions prepared in this way deposited crystals of the complex when left overnight at room temperature and this precluded study of reactions at lower temperatures where the half-lives were of the order of a few hours or more.

Results of kinetic runs are shown in Table I. Activation parameters (Table II) were obtained by least-squares analysis and uncertainties are standard deviations corrected in each case for the number of degrees of freedom.

Table I. First-Order Rate Constants for Decomposition of $Mn_2(CO)_8L_2$ in Decalin under an Atmosphere of O_2 ([Complex] = ca. 3 × 10^{-4} M)

L	T, °C	$10^6 k_{\mathrm{obsd}}$, s^{-1}
PEt_2Ph[a]	40.0	36.9, 37.7, 37.1
	49.9	195, 190, 190
	60.0	870,[b] 891, 882, 891
	70.0	3740, 3620, 3680
$PEtPh_2$[c]	30.0	13.2, 13.0, 13.2
	40.0	71.3, 72.7, 71.5
	50.0	356,[b] 355,[b] 360, 363
	60.0	1600, 1610, 1580
$P(p\text{-}MeOC_6H_4)_3$[d]	25.0	111, 109, 107
	35.0	588, 586, 592
	45.0	2710, 2730, 2570
$PPh(OMe)_2$[e]	70.0	10.7, 10.5, 10.3
	80.0	47.7, 48.7, 47.1
	90.0	213, 211, 216
	100.0	827,[b] 821,[b] 816, 814
$PPh_2(OMe)$[f]	50.0	14.5, 14.7, 14.6
	60.0	71.9, 71.1, 70.5
	70.0	309,[b] 300,[b] 311, 316, 313
	80.0	1290, 1280, 1300

[a] Followed at 1955 cm^{-1}. [b] Under air. [c] Followed at 1958 cm^{-1}. [d] Followed at 375 nm in stoppered silica cells, $[complex]_0$ = 1 × 10^{-4} M. [e] Followed at 1965 cm^{-1}. [f] Followed at 1963 cm^{-1}.

Table II. Activation Parameters for Homolytic Fission of $Mn_2(CO)_8L_2$ in Decalin

L	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\sigma(k_{\mathrm{obsd}})$, %
$PPhEt_2$	134.0 ± 0.4	97.8 ± 1.4	2.0
PPh_2Et	131.9 ± 0.2	96.4 ± 0.8	1.1
$P(p\text{-}MeOC_6H_4)_3$	123.6 ± 1.1	93.9 ± 3.5	3.4
$PPh(OMe)_2$	152.1 ± 0.6	101.7 ± 1.7	2.3
$PPh_2(OMe)$	138.7 ± 0.4	90.9 ± 1.3	1.8

Discussion

Detailed kinetic evidence for the occurrence of homolytic fission as the rate-determining step in a variety of reactions of $M_2(CO)_{10}$ and some axially substituted derivatives has been reviewed.[3b] These reactions include decomposition under O_2. This mechanistic assignment enabled the activation enthalpies for the reactions to be taken as a kinetic measure of the metal–metal bond strengths. In particular, excellent kinetic evidence for homolytic fission of $Mn_2(CO)_8(PPh_3)_2$ has been obtained[2c] and qualitative evidence for the process has been obtained[7] for $Mn_2(CO)_8(PEt_3)_2$ and $Mn_2(CO)_8\{P(OMe)_3\}_2$. It, therefore, seems reasonable to assign a homolytic fission mechanism to the reactions with O_2 of the very closely analogous complexes, the reaction kinetics of which are described here. The temperature dependence of the limiting rates under O_2 can therefore be taken as a measure of $\Delta H^{\ddagger}_{\mathrm{hf}}$, the activation enthalpy for homolytic fission.

Values of $\Delta H^{\ddagger}_{\mathrm{hf}}$ for the complexes $Mn_2(CO)_8L_2$ [L = $P(OMe)_3$, PEt_3, P-*n*-Bu_3, PPh_3, and $P(C_6H_{11})_3$] decrease almost

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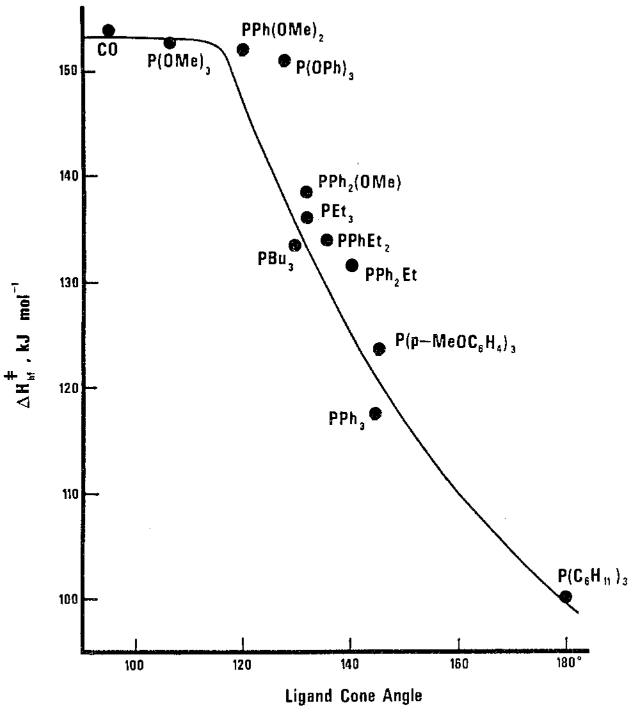

Figure 1. Dependence of $\Delta H^{\ddagger}_{hf}$ for $Mn_2(CO)_8L_2$ on the cone angle of L. The curve is intentionally drawn close to points for the symmetrical ligands PY_3.

linearly[3b] with increasing cone angle[8] of L. The values of $\Delta H^{\ddagger}_{hf}$ for the cases L = $PPh(OMe)_2$, $PPh_2(OMe)$, PEt_2Ph, $PEtPh_2$, and $P(p\text{-}MeOC_6H_4)_3$ fall on or around the same line and all the data presently available for such axially disubstituted complexes are shown in Figure 1. The line levels off at low cone angles as expected since steric effects are only likely to come into play when the size of L exceeds a critical value and this is likely to lead to a fairly sharp discontinuity. There is no reason that the plot should be linear and it has been drawn as a smooth curve passing through points for symmetrical ligands PY_3. Almost exactly analogous plots have been made of thermodynamic data for formation of Ni(0) complexes with P-donor ligands.[14]

The ligand $P(OPh)_3$ appears to be one of several[15] for which some compression is relatively much easier than for any of the other ligands involved in Figure 1. Its deviation from the trend set by the other ligands is therefore not surprising. $P(p\text{-}MeOC_6H_4)_3$ should have the same cone angle as PPh_3 and the values of $\Delta H^{\ddagger}_{hf}$ are quite close. $\Delta H^{\ddagger}$ for reaction of O_2 with $Mn_2(CO)_8(PPh_3)_2$ is 120.0 ± 0.6 kJ mol^{-1} and $\Delta H^{\ddagger}$ for reaction with CO is 117.2 ± 0.8 kJ mol^{-1}.[16] Some arguments have been offered for assigning the latter value to $\Delta H^{\ddagger}_{hf}$ although the difference is, fortunately, quite small and the question of assignment is not crucial. In any case, part of the difference between $\Delta H^{\ddagger}_{hf}$ for $Mn_2(CO)_8(PPh_3)_2$ and $Mn_2(CO)_8\{P(p\text{-}MeOC_6H_4)_3\}_2$ can be ascribed to electronic effects. $P(p\text{-}MeOC_6H_4)_3$ is more basic than PPh_3[10,17] and higher σ-donor character is known to increase the strength of the Mn–Mn interaction as measured by the value of $h\nu(\sigma \rightarrow \sigma^*)$.[3b,18] Up to 2 kJ of the difference could be ascribed to this electronic effect.

Electronic effects can be allowed for[3] by making use of a plot of $\Delta H^{\ddagger}_{hf}$ against $h\nu(\sigma \rightarrow \sigma^*)$. For a number of unsubstituted decacarbonyls, or mono- or disubstituted carbonyls containing smaller ligands, a fairly good linear plot is obtained, $\Delta H^{\ddagger}_{hf}$ increasing with $h\nu(\sigma \rightarrow \sigma^*)$ as expected if the latter is also a reasonable alternative estimate of the strength of the metal–metal bonds.[18] For those dimanganese complexes containing larger substituents, the values of $\Delta H^{\ddagger}_{hf}$ fall substantially below this line and the extent to which they do is given by $\Delta(\Delta H^{\ddagger}_{hf})$. Since the linear plot can be taken to describe what are electronically based effects on the strengths of the bonds, the values of $\Delta(\Delta H^{\ddagger}_{hf})$ are likely to be a more distinctive measure of steric effects than the values of $\Delta H^{\ddagger}_{hf}$ themselves. Values of $\Delta(\Delta H^{\ddagger}_{hf})$ for the complexes studied here are given in Table III together with some other particularly relevant values.

Table III. Steric Effects on $\Delta H^{\ddagger}_{hf}$

L	$h\nu$ $(\sigma \rightarrow \sigma^*)$, kJ mol^{-1}	$\Delta(\Delta H^{\ddagger}_{hf})$,[a] kJ mol^{-1}	cone angle, deg	Δ(hnp),[b] mV	ref
$P(OMe)_3$	342	−0.6 ± 0.4	107	520	3b
$PPh(OMe)_2$	337	+0.5 ± 0.6	120[c]	537[c]	this work
$PPh_2(OMe)_3$	329	−11.3 ± 0.4	132[c]	555[c]	this work
PPh_3	318	−26.5 ± 0.6[d] −29.3 ± 0.8[e]	145	573	3b 3b
$P(p\text{-}MeOC_6H_4)_3$	319	−23.7 ± 1.1	145[f]	439	this work
PPh_2Et	324	−16.5 ± 0.2	141[c]	400[c]	this work
$PPhEt_2$	329	−15.9 ± 0.4	136[c]	300[c]	this work
PEt_3	337	−15.7 ± 1.6	132	111	3b

[a] The observed value of $\Delta H^{\ddagger}_{hf}$ *minus* the value of $\Delta H^{\ddagger}_{hf}$ expected from Figure 2 in ref 3b. [b] Relative half-neutralization potentials for titration of free substituent ligand against perchloric acid in nitromethane. Basicity increases with decreasing Δ(hnp).[17] [c] By linear interpolation. [d] For reaction with O_2. [e] For reaction with CO. [f] Assumed equal to that for PPh_3.

Two series of steric effects of interest are $P(OMe)_3 \sim PPh(OMe)_2 < PPh_2(OMe) < PPh_3$ and $PEt_3 \sim PPhEt_2 \sim PPh_2Et < PPh_3$. Replacement of one group out of three identical groups attached to a P atom by one much larger group does not have an appreciable steric effect. Even replacement of a second group does not necessarily have an appreciable effect. We suggest that this reflects a more subtle operation of the steric effect than is allowed for by estimating the cone angles by simple interpolation. It has been pointed out that even P-donor ligands with three identical groups can have lowered effective cone angles because of a cog-like meshing of groups on different P atoms and without any strain necessarily being involved.[19] (This behavior should still, in principle, be observable through entropy parameters.) The cog-like nature of the ligands is well illustrated by their "ligand profiles" as derived from crystallographic studies.[11] This concept can be extended qualitatively to unsymmetrical P-donor ligands as follows.

It seems likely that when *one* group is replaced by a larger one, it can relatively easily be accommodated by being positioned in a plane that exactly bisects the angle between two of the equatorial CO ligands that are cis to the phosphine. The remaining smaller groups are then on planes such that two equatorial Mn–CO bond axes are each at an angle of 15° to those planes. This is probably not very different from the optimum arrangement for any P ligand with three identical groups. However, when the second group is replaced by a larger one, the most favorable arrangement will be if they are on two planes each making an angle of 30° to equatorial Mn–CO bond axes. In this case the remaining small group will be on a plane passing through an equatorial Mn–CO bond axis and this should not be too unfavorable. Replacing this last small group by a third larger one will, however, make this structure very unfavorable and a proportionately larger steric effect will be noticed. This general picture is borne out as shown in Figure 2. The straight line passes close to the values

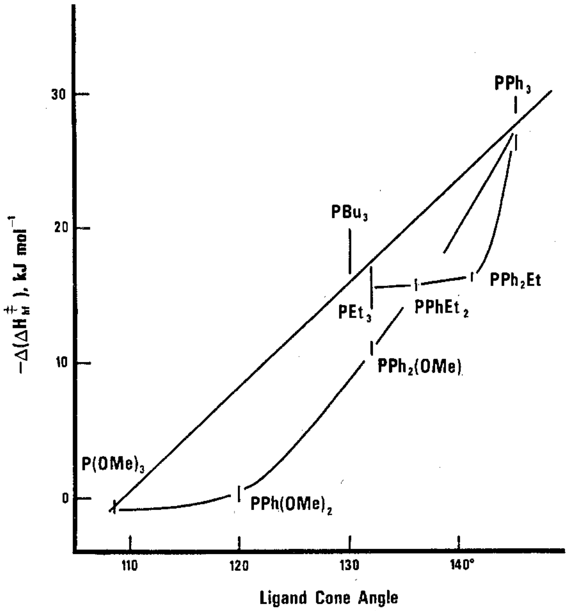

Figure 2. Dependence of $-\Delta(\Delta H^{\ddagger}_{hf})$ for $Mn_2(CO)_8L_2$ on the cone angle of L. Two values of $-\Delta(\Delta H^{\ddagger}_{hf})$ are given for L = PPh_3 (see Table III). The length of the vertical lines corresponds to ± the standard deviation of $-\Delta(\Delta H^{\ddagger}_{hf})$.

for those complexes containing P-donor ligands with three identical groups. It also passes close to the point for $Mn_2(CO)_8\{P(C_6H_{11})_3\}_2$ which is omitted for reasons of scale. It is clear that the steric effects for $PPhY_2$ and PPh_2Y (Y = MeO or Et) are indeed considerably less than expected from the linearly interpolated values of the cone angles. The sizes of these deviations are not, however, exactly as one might expect. It would seem that forcing an OMe group into the same plane as an equatorial Mn–CO bond axis would not be as unfavorable as forcing an Et group. If so then $-\Delta(\Delta H^{\ddagger}_{hf})$ for L = $PPh_2(OMe)$ should be lower than observed and $-\Delta(\Delta H^{\ddagger}_{hf})$ for L = PPh_2Et should be higher. However, this prediction probably involves overextending the application of what remains, after all, a very simple steric model. The general form of the results is certainly fully in accord with expectations. These arise essentially because of the lack of congruence between the threefold axis defined by the groups attached to the P atom and the fourfold axis defined by the equatorial CO ligands. This would not be the case for the corresponding complexes of $Co_2(CO)_6L_2$ when the equatorial CO ligands also define a threefold axis. It can therefore be predicted that linear interpolation of cone angles should be perfectly satisfactory for these complexes for which there have been preparations[20] but for which values of $\Delta H^{\ddagger}_{hf}$ have not yet been determined. Some slight indication of a better meshing of $P(C_6H_{11})_3$ in $Co_2(CO)_6\{P(C_6H_{11})_3\}_2$ than in $Mn_2(CO)_8\{P(C_6H_{11})_3\}_2$ has been inferred from spectroscopic studies.[18] None of these considerations is affected by the values of the cone angles taken for $P(OMe)_3$, PEt_3, or PPh_3 since the question is simply whether data for the intermediate, "mixed" ligands interpolate linearly or not. The fact that PPh_3 has had a cone angle of 155° or greater assigned to it[21] is consequently not of any relevance here.

One final comment on the steric effect can be made. The $AsPh_3$ ligand is generally believed to be smaller than PPh_3.[22] For the value of $\Delta(\Delta H^{\ddagger}_{hf})$ for $Mn_2(CO)_8(AsPh_3)_2$ (−13.4 ± 2.4 kJ mol^{-1})[3b] to lie within one standard deviation of the linear plot in Figure 2, the cone angle of $AsPh_3$ would have to be between 124 and 130°. This range is related solely to the standard deviation of $\Delta(\Delta H^{\ddagger}_{hf})$. The actual uncertainty in the cone angle would have to be somewhat larger because of some uncertainty as to how the straight line should be drawn, but a reasonable estimate of the cone angle would seem to be 127° with a maximum uncertainty of ±8°.

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Registry No. $Mn_2(CO)_8(PEt_2Ph)_2$, 15444-75-4; $Mn_2(CO)_8(PEtPh_2)_2$, 15444-76-5; $Mn_2(CO)_8(P(p\text{-}MeOC_6H_4)_3)_2$, 15662-85-8; $Mn_2(CO)_8(PPh(OMe)_2)_2$, 61943-30-4; $Mn_2(CO)_8(PPh_2(OMe))_2$, 61943-35-9.

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(8) The cone angles used in this plot are those originally reported by Tolman et al. as obtained from molecular models.[9] Some of these have subsequently been modified[10] on various grounds. Thus, the original cone angle of P-*n*-Bu_3 (130°) was increased by 2° on the grounds that it was not reasonable for it to be less than that for PEt_3 (132°). The cone angle of 179 ± 10° for $P(C_6H_{11})_3$ was reduced to 170° on the basis of some equilibrium studies although the uncertainty is still ca. ±10°. This sort of piecemeal adjustment seems to us to confuse the essential simplicity of the original approach by the adjustment of only some of the values according to empirical results and without any real gain. Crystallographic studies have shown that the detailed environment of $P(C_6H_{11})_3$ in a complex can affect its actual cone angle appreciably.[11] In particular it can be as low as 163° in sterically congested complexes such as $\{P(C_6H_{11})_3\}_2PtI_2$.[12] While such data demonstrate the inherent compressibility of the ligand, they provide no indication of the cost of such compression in terms of increased internal energy of the complex. Only kinetic or thermodynamic studies can do this. Thus the steric inhibition known to occur for nucleophilic substitution reactions by $P(C_6H_{11})_3$[13] will be expected to be greater the more highly coordinated the center at which attack occurs, and this appears to be true. Crystallographic cone angles should be used only when the ligands in the complex are demonstrably uncompressed, and on this basis, the original cone angle of 179° for $P(C_6H_{11})_3$ is clearly preferable.[11] In this way any deviations of kinetic or thermodynamic data from regular trends with changing electronic properties of the ligands, for instance, can be ascribed to unfavorable steric effects that manifest themselves either through changed enthalpies (caused by the compression of the ligand) or through changed entropies (caused by more restricted ways in which the ligand can fit).

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