

Interconversion of MeReO(dithiolate)(NC₅H₄-X) and MeReO(dithiolate)(PAr₃) complexes: The equilibrium constants follow the Hammett equation but the rate constants do not †

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Equilibration occurs among the species MeReO(dithiolate)Py, MeReO(dithiolate)(PZ₃), Py, and PZ₃ where the chelating dithiolate ligand is 1,2-ethanedithiol (edt) or 1,3-propanedithiol (pdt), Py stands for NC₅H₄-4-X and PZ₃ for both P(C₆H₄-4-Y)₃ and P(alkyl)_n(Ph)_{3-n}. Equilibrium constants in the pdt series were evaluated directly; values of *K* generally favor phosphane coordination and range from 4.8 × 10⁻² (X = NMe₂, Y = Cl) to 3.2 × 10⁴ (X = CN, Y = OMe). The values of *K* are well correlated by the Hammett equation with ρ_X^K = 2.7(3) and ρ_Y^K = -2.0(3). Kinetic data were determined with the stopped-flow method for 65 reactions of the edt and pdt complexes, and resolved into forward and reverse components by use of the equilibrium constants. Values of *k*_{for} deviate markedly from Hammett behavior, especially along any series with a given X substituent, where plots of log *k*_{for} against 3σ_Y take on a V-shaped appearance. This pattern has been interpreted in terms of a two step mechanism for ligand substitution reactions of these complexes. The rate constants for those phosphanes that are the better Lewis bases are governed by Re–P bond formation. The rate constants for those phosphanes that are weaker Lewis bases, on the other hand, are governed by the second step in which an initial ψ-octahedral complex rotates towards a transition state that is an approximate trigonal prism. In so doing, the prior Re–P interaction is weakened, which gives rise to an increase in log *k*_{for} with σ_Y.

Introduction

Ligand substitution reactions of five-coordinate, square-pyramidal methyl(oxo)rhenium(v) dithiolate complexes can be represented by the equation^{1,2}



In this notation, dt represents 1,2-ethanedithiolate (edt), 1,3-propanedithiolate (pdt), or 2-(mercaptomethyl)thiophenolate (mtp) and the ligands Lⁱ and L^j may be, for example, phosphines or pyridines.^{3–8} Structural formulas are shown in Chart 1.

Our interest in this family of reactions has been sustained by two factors. First, they are intimately involved in the mechanism of rhenium-catalyzed oxygen-atom transfer reactions (YO + X → Y + XO).^{2,9–13} Second, they present a fundamental issue of mechanism that appears unique to this structure, in that no direct route is available to the symmetric transition state that is necessary for an associative mechanism for substitution

which also satisfies the principle of microscopic reversibility. This unusual aspect was explored in our earlier research,¹⁴ and it will be amplified in the Discussion section, on the basis of the new results and their mechanistic analysis.

Two examples of this reaction have been explored previously. The seemingly simpler one is pure exchange itself, between MeReO(edt)Pyⁱ and Pyⁱ. These are rapid reactions that were studied by NMR line broadening. In every case, pyridine exchange follows second-order kinetics and proceeds with an associative mechanism.¹⁵ A more telling example of ligand substitution (which further established that the Py exchange process does not proceed in a single-step) is provided by reactions between MeReO(mtp)(PZ₃) and PY₃, where Z and Y include aryl and alkyl groups. In this case substitution proceeded in two steps with the intervention of easily detected concentrations of the intermediate [MeReO(mtp)(PY₃)]*, a geometric isomer of the final product.¹⁴

In the present study we have undertaken a study of the reactions of complexes bearing edt and pdt ligands, to avoid sequential reactions of geometrical isomers. Important as this aspect was in the mtp case, the complicating factor of observable sequential reactions of geometrical isomers can be eliminated by use of a symmetric dithiolate. This study thus

† Electronic supplementary information (ESI) available: Additional plots of kinetic data and analysis. See <http://www.rsc.org/suppdata/dt/b3/b306634g/>

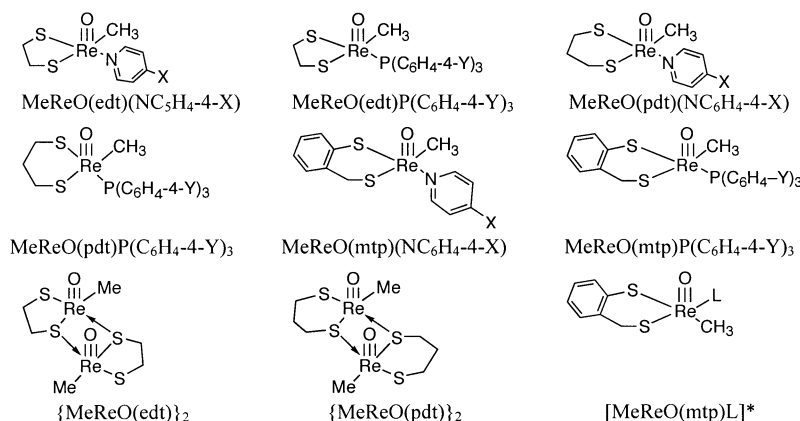


Chart 1 Structural formulas of methyl(oxo)rhenium(v) dithiolates.

entailed direct equilibrium and kinetic measurements on the reaction



where PZ_3 denotes a generalized phosphane ($Z = \text{aryl, alkyl}$; often $\text{P}(\text{C}_6\text{H}_4\text{-}4\text{-Y})_3$), Py a generalized pyridine, $\text{NC}_5\text{H}_4\text{-}4\text{-X}$, and the dithiolates edt or pdt . The symmetry of the intermediate precludes a second step being detectable, $[\text{MeReO(dt)(PY}_3)]^*$ and $[\text{MeReO(dt)(PY}_3)]$ being enantiomers not geometrical isomers. Nonetheless, there will still be two steps in reaching the transition state. They respond differently to substituent groups X and Y on the ligands, however, which gives rise to non-Hammett behavior as one step or the other becomes rate-controlling.

Experimental

General

Methyl(oxo)rhenium(v) dithiolate dimers, $\{\text{MeReO(edt)}\}_2$ and $\{\text{MeReO(pdt)}\}_2$, were synthesized according to literature procedures⁴ from 1,2-ethanedithiol (edtH_2) or 1,3-propanedithiol (pdtH_2) and $\{\text{MeReO(SPh)}_2\}_2$. The latter compound was prepared from MeReO_3 and PhSH , as reported.¹⁶ Pyridines and phosphanes were purchased (Aldrich or Strem) and used as received. Benzene (ACS grade, Aldrich) was used as the solvent for UV-visible spectroscopy. Solutions of either $\text{MeReO(dt)(NC}_5\text{H}_4\text{-}4\text{-X})$ complex in C_6H_6 or C_6D_6 were prepared by adding an excess of that pyridine in a solution of the dimer. An excess of pyridine was maintained to ensure that the no dimeric compound remained.^{6,17} The mononuclear complexes were identified by NMR spectroscopy in comparison with spectra determined previously.⁴

Equilibrium studies

Values of K_1 were determined by UV-visible spectrophotometric titration only for the pdt complexes. A concentration in the range of 10–500 mM of the given Py ligand was placed in a 1 cm path UV-visible cell containing 0.05 mM $\{\text{MeReO(pdt)}\}_2$. The spectrum was recorded using a Shimadzu UV 3101PC spectrophotometer after the addition of each 10 μL portion of a solution of PAR_3 . This procedure was repeated until the spectra remained unchanged with further addition of PAR_3 . The software PSEQUAD¹⁸ was used to analyze the multi-wavelength absorbance data to obtain the equilibrium constant. These calculations are based on the net absorbance change from beginning to end of the addition of PAR_3 . Typically, absorbance readings were recorded at 10 different wavelengths in the 400–600 nm range; this set of values was used in a global fit to extract the equilibrium constant for selected pyridine and phosphane derivatives.

Kinetics

Rate constants for reaction (2) were obtained by the use of an OLIS stopped-flow instrument equipped with a Rapid Scanning Monochromator system set for the range 350–500 nm. The absorbance readings monitor the decrease of absorbance at 350–395 nm, in the particular instance of $\text{C}_5\text{H}_5\text{N}$ and PPh_3 , where $\epsilon_{\text{RePy}} > \epsilon_{\text{RePAR}_3}$ and the simultaneous increase at 395–415 nm, where the reverse inequality holds. A persistent isosbestic point for this pair was found at 395 nm which showed that no intermediate attains an appreciable concentration during the reaction. The same was true for the other pyridine-phosphine combinations, save for small differences in the wavelengths cited. Circulating thermostated water was used to control the temperature at $25.0 \pm 0.2^\circ\text{C}$.

A typical experiment involved mixing equal volumes of benzene solutions containing 20.0 mM PPh_3 and 0.1 mM $\text{MeReO(edt)(NC}_5\text{H}_5)$ containing 20.0 mM $\text{C}_5\text{H}_5\text{N}$. The excess

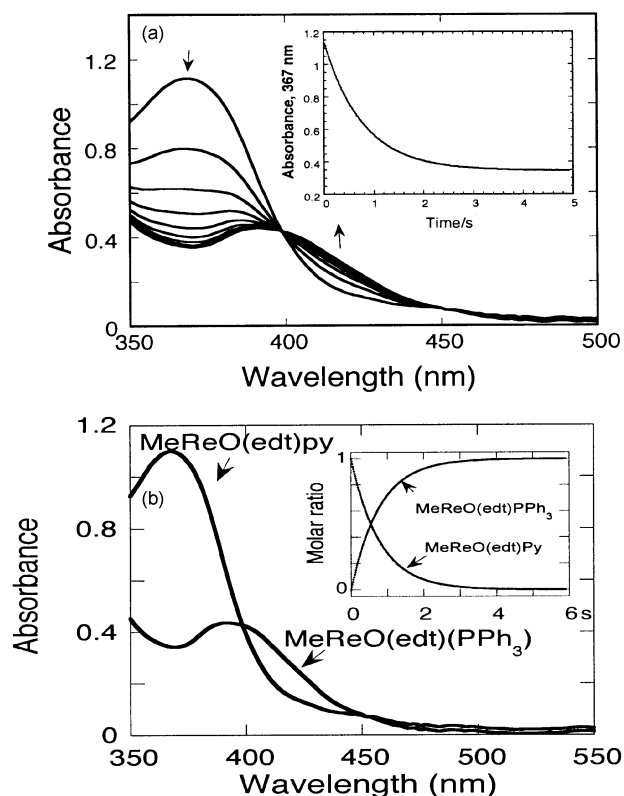


Fig. 1 Upper: Stopped flow kinetic data showing repetitive scans of reaction 1 with these conditions: 0.05 mM $\text{MeReO(edt)(NC}_5\text{H}_5)$, 10.0 mM PPh_3 and 10.0 mM Py in C_6H_6 at 25°C . Data were collected over a total time of 5.0 s at intervals of 0.0125 s; for sake of clarity only scans at 0.1 s intervals are shown. The inset shows a fit to first-order kinetics of the data extracted at 367 nm. Lower: The results of a global fit of the kinetic data by the singular value decomposition method, showing the spectra of reactant and product separately resolved by this analysis and an inset in which the spectra have been resolved into their reactant and product components, expressed as molar ratios.

of pyridine was used to prevent formation of the parent dimer, $\{\text{MeReO(edt)}\}_2$. The rapid-scan spectra for this particular experiment are shown in Fig. 1. Reaction (2) proceeds nearly to completion with these concentrations.

Results and discussion

Equilibrium constants

Values of K were determined for 11 reactions of the pdt complexes for 10 pairs of Py and PZ_3 derivatives: ($X = \text{NMe}_2$, $Y = \text{OMe}$), ($X = \text{NMe}_2$, $Y = \text{Me}$), ($X = \text{OMe}$, $Y = \text{Me}$), ($X = \text{OMe}$, $Y = \text{H}$), ($X = \text{Me}$, $Y = \text{H}$), ($X = \text{Me}$, $Y = \text{F}$), ($X = \text{H}$, $Y = \text{F}$), ($X = \text{H}$, $Y = \text{Cl}$), ($X = \text{CHO}$, $Y = \text{Cl}$), ($X = \text{Ac}$, $Y = \text{Cl}$), ($X = \text{CN}$, $Y = \text{Cl}$). The values of K , which have been determined to a precision of *ca.* 10%, are given in Table 1. The remaining 24 values of K are redundant and were calculated directly or indirectly from these eleven experimental values; of course the calculated ones will have higher error limits owing to the propagation of errors. The general formula is as given in eqn. (4) for the equilibrium



$$K_{A,B} = \frac{K_{A,Y} \times K_{X,B}}{K_{X,Y}} \quad (4)$$

This particular equilibrium illustrates the procedure:

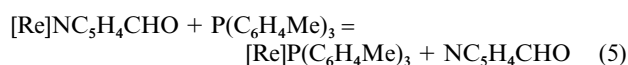


Table 1 Equilibrium constants^a for reactions between MeReO(pdt)(NC₅H₄-4-X) and P(C₆H₄-4-Y)₃ in C₆H₆ at 25 °C

X↓ Y →	K				
	OMe	Me	H	F	Cl
NMe ₂	8.2 ± 0.8	2.1 ± 0.2	0.40	0.14	0.048
OMe	300	78 ± 7	15 ± 1	5.2	1.8
Me	340	88	17 ± 1	5.9 ± 0.6	2.0
H	1300	330	63	22 ± 2	7.4 ± 0.7
CHO	(4700)	1200	230	80	27 ± 2
C(O)Me	(3700)	930	180	62	21 ± 2
CN	(32000)	8000	1500	530	180 ± 20

^a Experimental values are given in boldface; the others are redundant values of *K* calculated from them according to eqns. (4)–(6) as explained in the text. Standard deviations of the calculated entries are obtained by the law of propagation of errors. Values enclosed parenthetically have errors nearly as large as the entries themselves.

The equilibrium constant for reaction (3), *K*(CHO,Me) is arrived at in these steps:

$$K(\text{Me, Me}) = \frac{K(\text{Me, H}) \times K(\text{OMe, Me})}{K(\text{OMe, H})} = \frac{17 \times 78}{15} = 88 \pm 19 \quad (6)$$

where the standard deviation was calculated from those of the components. In Table 1, 11 values of *K* derive from experiments, 9 can be calculated from three experimental values, and the remaining three by combining experimental and calculated values. Naturally, the latter group have the largest error limits.

Not surprisingly, the largest *K* is 3.2×10^4 for NC₅H₄CN, which has the most electron-withdrawing substituent, in combination with P(C₆H₄OMe)₃, with the most electron releasing substituent. Likewise, the smallest *K* value is 0.048 for the reaction between [Re]NC₅H₄NMe₂ and P(C₆H₄Cl)₃.

Kinetic data

Reaction (2) was studied with an excess of the pyridine present, usually at a concentration of 10 mmol L⁻¹, to prevent complications arising from the presence of the dimer {MeReO(pdt)}₂, were the following equilibrium to proceed to the right to any substantial extent,



The phosphanes were also used in excess over rhenium, such that both [Py] and [PAR₃] remained constant in any experiment. The rate of approach to equilibrium is reaction (2) can be written as follows, with (Re) standing for MeReO(pdt)

$$-\frac{d[(\text{Re})\text{Py}]}{dt} = k_{\text{for}}[(\text{Re})\text{Py}][\text{PAR}_3] - k_{\text{rev}}[(\text{Re})\text{PAR}_3][\text{Py}] \quad (8)$$

The rate constant for equilibration thus becomes

$$k_e = k_{\text{for}}[\text{PAR}_3] + k_{\text{rev}}[\text{Py}] \quad (9)$$

With incorporation of *K* from Table 1, this expression is obtained

$$k_e = k_{\text{for}} \times \{[\text{PAR}_3] + [\text{Py}]K^{-1}\} \quad (10)$$

Thus a plot of *k_e* against {[PAR₃] + [Py]*K*⁻¹} represents the equation of a straight line that passes through the origin. The least-squares fit to eqn. (10) gave values of *k_{for}* that are summarized in Table 2.

Reactions of MeReO(edt)Py required a different analysis because *K* was not independently evaluated. Eqn. (10) was also used for the data analysis, but with both *k_{for}* and *K* treated as adjustable parameters. The values of *k_{for}* are given in Table 3. The equilibrium constant is often so large that the second term

Table 2 Rate constants (*k_{for}*/L mol⁻¹ s⁻¹) for reactions between MeReO(pdt)(NC₅H₄-4-X) and P(4-YC₆H₄)₃ in C₆H₆ at 25 °C^a

X↓ Y →	OMe	Me	H	F	Cl
NMe ₂	—	—	28.8 ± 0.3	—	—
OMe	157 ± 2	91 ± 1	78 ± 1	137 ± 2	156 ± 2
Me	137 ± 2	82 ± 1	71 ± 1	121 ± 2	136 ± 2
H	190 ± 2	114 ± 2	103 ± 1	166 ± 2	182 ± 3
CHO	368 ± 5	235 ± 2	171 ± 2	162 ± 3	179 ± 5
C(O)Me	340 ± 7	201 ± 2	154 ± 2	166 ± 4	197 ± 3
CN	760 ± 20	477 ± 5	401 ± 6	251 ± 3	281 ± 3

^a Values of *k_{for}* were obtained by fitting *k_e* to eqn. (10) with *K* from Table 1.

in eqn. (10) does not contribute. For the case where *k_{rev}* does contribute, *K* could be determined, as given in Table 4. Although these values have considerable uncertainties associated with them, the trend is clear that *K_{edt}* > *K_{pdt}*. Perhaps this is so because the five-membered ring of edt is nearly co-planar, whereas the six-membered with pdt adopts a chair conformation that makes ligand attachment more difficult, especially for large phosphines.

Reactions of a selected group of other phosphanes were also studied, with the results presented in Table 5. Presented along with the rate constants are the cone angles and p*K_a* values of the conjugate acids of the phosphanes.¹⁹ Although PMePh₂ and P(C₆H₄-4-OMe)₃ have the same value of p*K_a*, the rate constant of ligand substitution of the former is 55 times faster than that of the latter owing to the effect of steric hindrance, as indicated by a bigger cone angle, 145°.

Temperature profiles. The temperature dependence of the reaction between MeReO(edt)Py and PPh₃ was studied over the temperature range of 283–323 K. Activation parameters were calculated from the least-squares fit of ln(*k*/*T*) against 1/*T*; Δ*H*[‡] = 24.0 ± 0.5 kJ mol⁻¹ and Δ*S*[‡] = -124 ± 2 J mol⁻¹ K⁻¹. The large negative activation entropy indicates an associative pathway,^{20–23} which is compatible with earlier findings which have demonstrated that the rate depends directly on the identity and concentration of the incoming ligand.¹⁴

Substituent effects

Equilibrium constant. One must take into account the effects of variations of substituents X on Py and Y on PAR₃, which act in concert. According to studies of multiple-substituent effects in organic chemistry,^{24–27} a correlation was made using the Hammett substituent constants, taken from the compilation of Brown and Okamoto²⁸ for the substituent constants of X and Y in the overall expression:

$$\log K(X, Y) = \log K_{\text{ref}} + \rho_X^K \times \sigma_X + \rho_Y^K \times (3\sigma_Y) \quad (11)$$

Table 3 Rate constants ($k_{\text{for}}/\text{L mol}^{-1} \text{s}^{-1}$) for reactions between $\text{MeReO}(\text{edt})(\text{NC}_5\text{H}_4\text{-4-X})$ and $\text{P}(\text{4-YC}_6\text{H}_4)_3$ in C_6H_6 at 25°C

$\text{X}\downarrow\text{Y}\rightarrow$	OMe	Me	H	F	Cl
NMe_2	91 ± 1^a	50.5 ± 0.7^a	39.9 ± 0.4^b	150 ± 20^b	—
OMe	227 ± 5^a	120 ± 2^a	96 ± 2^a	143 ± 2^b	186 ± 1^a
Me	205 ± 6^a	111 ± 2^a	91 ± 1^b	133 ± 2^b	148 ± 5^b
H	300 ± 20^a	152 ± 2^a	128 ± 2^b	179 ± 2^a	160 ± 10^b
CHO	530 ± 20^a	284 ± 3^a	208 ± 2^a	168 ± 2^a	189 ± 4^a
$\text{C}(\text{O})\text{Me}$	480 ± 10^a	258 ± 6^a	195 ± 2^a	174 ± 2^a	211 ± 2^a
CN	1190 ± 40^a	591 ± 6^a	480 ± 8^a	279 ± 8^a	251 ± 3^a

^a Values of k_e were analyzed according to eqn. (10), with the term $[\text{Py}]K^{-1}$ omitted. ^b The term $[\text{Py}]K^{-1}$ of eqn. (10) was retained.

Table 4 Equilibrium constants for reactions of $\text{MeReO}(\text{edt})(\text{NC}_5\text{H}_4\text{-4-X})$ with $\text{P}(\text{C}_6\text{H}_4\text{-4-Y})_3$ at 25°C in benzene^a

$\text{X}\downarrow\text{Y}\rightarrow$	H	F	Cl
Me_2N	2.5 ± 0.2	3.0 ± 1.8	—
MeO	7 ± 4	18 ± 5	—
Me	36 ± 29	38 ± 12	11 ± 4
H	—	—	8 ± 4

^a From fitting of kinetic data to eqn. (10).

Table 5 Rate constants of reactions between $\text{MeReO}(\text{edt})(\text{NC}_5\text{H}_5)$ and other phosphanes in C_6H_6 at 25°C

PZ_3	$\theta/^\circ$	$\text{p}K_a$	$k/\text{L mol}^{-1} \text{s}^{-1}$
PCyPh_2	153	5.05	2.30×10^2
PCy_2Ph	162	—	3.01×10^1
PMePh_2	136	4.57	1.42×10^4
$\text{P}(\text{C}_6\text{H}_4\text{-4-OMe})_3$	145	4.57	2.57×10^2
$\text{P}(\text{MeO})_3$	107	2.60	$> 4 \times 10^4$

The factor σ_Y includes a multiplying factor of three for $\text{P}(\text{C}_6\text{H}_4\text{Y})_3$. The fitted reaction constants for K are symbolized by ρ_X^K and ρ_Y^K . For this analysis only the 11 experimental data from Table 1 were used, because the remaining values of K were calculated ones whose inclusion would not enhance the analysis. The reaction constants were obtained by use of the least-square program SCIENTIST²⁹ which allows for the use of two independent variables from the fit, $\rho_X^K = 2.2 \pm 0.3$ and $\rho_Y^K = -1.5 \pm 0.3$. These parameters have opposite signs, of course, because pyridine is coordinated to the reactant, phosphane to the product. In this calculation $\log K(\text{H,H})$ was also allowed to float, the refined value being 1.58 ± 0.09 , as compared to the experimental value 1.80 ± 0.11 . Given the error, the internal consistency is adequate, as illustrated in Fig. 2 by a plot of $\log(K_{\text{calcd}}$ vs. K_{exp}) which has a 45° slope.

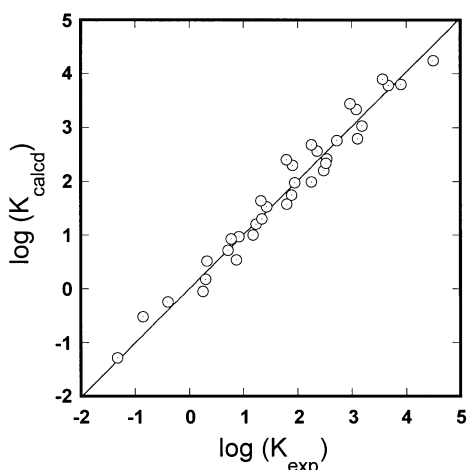


Fig. 2 Illustrating the agreement between experimental (Table 1) and Hammett-correlated values of the equilibrium constants for reactions between $\text{MeReO}(\text{pdt})(\text{NC}_5\text{H}_4\text{-4-X})$ and $\text{P}(\text{C}_6\text{H}_4\text{-4-Y})_3$. The least-squared line has a slope of 1.01.

In a second treatment, $K(\text{H,H})$ was fixed at the experimental value, which resulted in these reaction constants, $\rho_X^K = 2.7 \pm 0.3$ and $\rho_Y^K = -2.0 \pm 0.3$, which are not significantly different. The reaction constants reflect the entering and leaving groups. Including the calculated but no less valid values of K in Table 1, the entire range of equilibrium constants spans a factor of 6.7×10^5 , which indicates that the difference between reactant and product is quite sensitive to substituents.

Rate constants. The entries in Tables 2 and 3 indicate that factors other than simple electronic effects on a single rate constant come into play. For one thing, the span of rate constant values for the same X, Y substituent pair is considerably narrower than that for K . For example, values of k_{for} in Table 2 vary by but a factor of 30, as compared to a range of 8×10^4 in K , the same ligands considered. Further, the span of the rate constants with variation of the Y substituent is narrower than that for the variation of the X substituent, which reverses the trends for the equilibrium constants.

Even more strikingly, the k_{for} values show unusual trends. The small reversal of the ordering of rate constants in each column of Table 2 is barely significant. But the falling and rising of the values in each row with variation of Y is rather pronounced. The same pattern held for every Y group. Put another way, a plot of $\log k_{\text{for}}$ versus σ_Y , for any given substituent X on Py, shows a distinctive V-shape. Fig. 3 depicts these nonlinear Hammett plots for a few of the reactions.

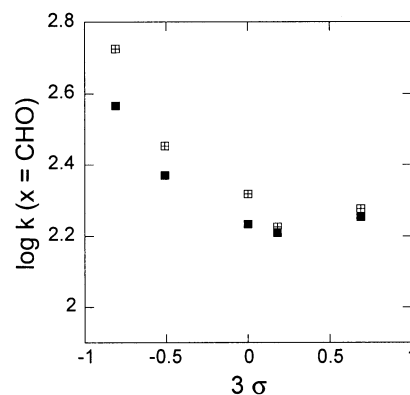
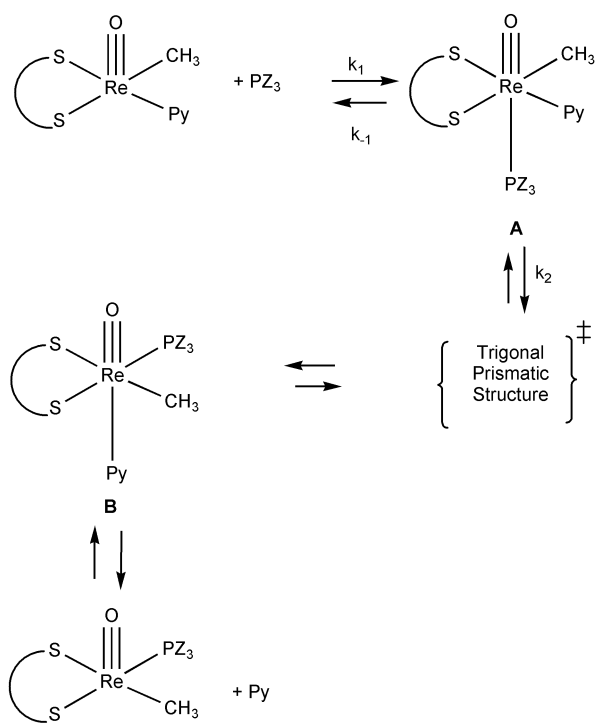


Fig. 3 Hammett plots of $\log k$ for the reactions of $\text{MeReO}(\text{dt})[\text{NC}_5\text{H}_4\text{-4-CHO}]$ with different $\text{P}(\text{C}_6\text{H}_4\text{-4-Y})_3$ compounds for $\text{dt} = \text{edt}$ (hatched squares) and pdt (filled squares) showing the non-linear relationship indicative of a sequential-step mechanism.

In the Introduction, a complex mechanism was mentioned. Our depiction of that mechanism is given in Scheme 1, involving multiple steps: PZ_3 approaches the rhenium from the vacant axial position to form a six-coordinate intermediate A; a Bailar twist transfers A to its geometric isomer B; Py departs from B to generate the final product.^{30,31} The coordination number of rhenium complexes can easily vary from five to six. Bailar twist has been already proved to be a common isomerization pathway for certain six-coordinate transition metal complexes.³²⁻³⁷ The justification for such an elaborate scheme, and



Scheme 1 Two step mechanism for ligand substitution.

the data that support it (which include the spectroscopic detection of intermediate A) have been presented earlier.¹⁴ Given this mechanism as a premise, the expression for the rate constant is

$$k_{\text{for}} = \frac{k_1}{1 + k_{-1}/k_2} \quad (12)$$

There are two limiting forms of eqn. (1). One identifies k_{for} as k_1 , which will be the case when $k_2 \gg k_{-1}$. In that case the first step is rate-controlling, and the second much more rapid in comparison. Whether the limit is actually realized is not the major issue; if it is, or nearly is, the rate will be governed by bond-making between Re and the incoming phosphane ligand. As such, the “ordinary” nucleophilic effect will be seen, and the more electron-donating Y is, the faster the reaction. This is evidently the case for Y = MeO and Me, for example.

The other limit has $k_{\text{for}} = (k_1/k_{-1})k_2$, in which case the first step is at equilibrium and the second is rate-controlling. When $\text{P}(\text{C}_6\text{H}_4\text{-4-Y})_3$ is less nucleophilic, as with Y = F and Cl, then the first step will feature a small binding constant, $k_1/k_{-1} \ll 1$; moreover, the weakly-bound phosphine will leave more rapidly than the turnstile rotation step; that is, $k_{-1} \gg k_2$. Because k_2 governs the substituent effect under those circumstances, the reaction constant will show a rising effect with σ_Y as coordination of the bulky phosphane group weakens as the molecule approaches the configuration of a trigonal prism because the ligands must rotate past one another. Again, the equilibrium constants for the same reaction conform to an ordinary Hammett relationship because only the initial and final states of the system come under consideration, not the special intermediate.

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