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Preliminary communication

The role of SO_2 as a ligand to mediate associative substitution reactions of some 18-electron molybdenum complexes [☆]

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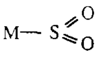
Abstract

Results of kinetic studies are reported for intramolecular PPh_3 substitution reactions of $Mo(CO)_2(\eta^1\text{-L})(PPh_3)_2(SO_2)$ to form $Mo(CO)_2(\eta^2\text{-L})(PPh_3)(SO_2)$ (L = dmpe=$(Me)_2PC_2H_4P(Me)_2$ and dppe=$Ph_2PC_2H_4PPh_2$) in THF as solvent. Activation parameters for the reactions are: $\Delta H^{\neq}$ values 12.3 kcal mol^{-1} for dmpe and 16.7 kcal mol^{-1} for dppe; and $\Delta S^{\neq}$ values −30.3 cal mol^{-1} K for dmpe and −16.4 cal mol^{-1} K for dppe. These results are consistent with an intramolecular associative mechanism. The facile associative pathway for the reaction is discussed in terms of the ability of SO_2 to accept a pair of electrons from the metal, with a bonding transformation of η^2-SO_2 to η^1-pyramidal SO_2, so maintaining a stable 18-electron count for the complex in the transition state.

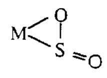
Keywords: Molybdenum; Sulfur dioxide; Ligand substitution; Kinetics; Mechanism

Tolman's [1] 16-, 18-electron rule suggests that 18-electron monomeric organometallic compounds undergo ligand substitution via a dissociative pathway involving a 16-electron intermediate rather than by the higher energy 20-electron intermediate required by an associative mechanism. Yet it had earlier been reported [2] that the presence of certain ligands (NO, cyclopentadienyl, and benzene) permits associative substitution reactions by localizing a pair of electrons on the ligand in the transition state for reaction, and so maintaining the stable 18-electron count throughout the reaction pathway. Considerable research has been carried out on the ring metal compounds in terms of ring-slippage processes [3], but more closely related to SO_2 is the NO ligand. It can either be bonded to a metal in a linear fashion M=N=O, or a pair of non-bonding electrons can be localized on the nitrogen to give a bent sp^2 hybrid nitrosyl [4] $M\text{-}\overline{N}\text{=}O$. This then frees a metal orbital for attack by the entering nucleophile and results in a low-energy associative displacement reaction via a stable 18-electron transition state [2].

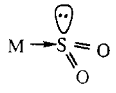
It has long been known [5] that SO_2 is both a Lewis acid and a Lewis base, with metal-SO_2 bonding modes of the types [6] η^1-planar (see **I**) or η^2 (see **II**) geometries in which it behaves as a Lewis base, donating a pair of electrons to the metal accompanied by π-back-bonding from filled d-orbitals of the metal atom. Also the Lewis acid behavior of SO_2 as a ligand results in an η^1-pyramidal (see **III**) bonding mode, in which SO_2 accepts a pair of electrons from the metal.



I

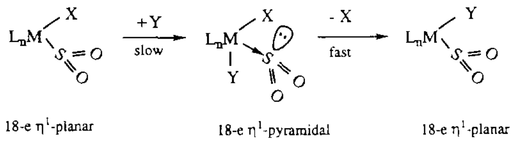


II



III

These bonding modes suggest that the ligand SO_2 may possibly, like NO, mediate an associative displacement reaction of an 18-electron monomeric organometallic compound. The presumed reaction mechanism is depicted in a general form in Eq. (1).



(1)

[☆] This article is dedicated to Fausto Calderazzo on his 65th birthday.

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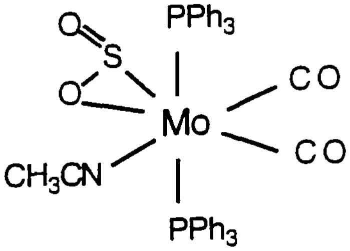
This hypothetical case shows that as SO_2 shifts from Lewis base to Lewis acid behavior, the entering nucleophile Y is enabled to attack the metal while a stable 18-electron count is maintained for the active intermediate. In spite of the seeming plausibility of this ligand substitution mechanism, there seems to have been no report of its observation.

We present here preliminary results of a kinetic study that appear to be best explained on the bases of an $\eta^2 \rightarrow \eta^1$-pyramidal $\rightarrow \eta^1$-planar mechanism. The compound investigated was *cis,trans*-$Mo(CO)_2(PPh_3)_2(\eta^2\text{-}SO_2)(NCCH_3)$ [7] (see **IV**), and its reactions with dppe ($Ph_2PC_2H_4PPh_2$) and with dmpe ($((Me)_2PC_2H_4P(Me)_2$ were studied in THF solution.



IV

The good leaving group CH_3CN is rapidly replaced at low temperature, initially affording $Mo(CO)_2(\eta^1\text{-L})(PPh_3)_2(SO_2)$ (Eq. (2)), which is believed to contain η^2-SO_2 [7].

$$Mo(CO)_2(PPh_3)_2(SO_2)(NCCH_3) + L \longrightarrow Mo(CO)_2(\eta^1\text{-L})(PPh_3)_2(SO_2) + CH_3CN \quad (2)$$

The η^1-L complex thus formed then undergoes intermolecular PPh_3 substitution and chelating ring closure more slowly to form $Mo(CO)_2(\eta^2\text{-L})(PPh_3)(SO_2)$ [8*] (Eq. (3)).

$$Mo(CO)_2(\eta^1\text{-L})(PPh_3)_2(SO_2) \longrightarrow Mo(CO)_2(\eta^2\text{-L})(PPh_3)(SO_2) + PPh_3 \quad (3)$$

The PPh_3 substitution [9*] is first-order with respect to the concentration of the η^1-L complex. Rate constants and activation parameters are given in Table 1.

The low values of $\Delta H^{\neq}$ and the negative values of $\Delta S^{\neq}$ are indicative of nucleophilic attack on the metal and an associative mechanism. This could result from the diving force provided by closure of the diphos chelate ring in going from η^1-L to the η^2-L species. Arguing against this is the earlier report [10] that CO substitution reactions of $Mo(CO)_5(\eta^1\text{-L})$ (L = dppe or dmpe) involving formation of $Mo(CO)_4(\eta^2\text{-L})$ have near zero $\Delta S^{\neq}$ values (-1.7 cal mol^{-1} K for dmpe and 3.3 cal mol^{-1} K for dppe) and large $\Delta H^{\neq}$ values (28.7 kcal mol^{-1} for dppe and 28.2 kcal mol^{-1} for dmpe), indicating primarily a dissociative process. If a nucleophilic attack on the metal made a major contribution to the chelate ring closure then one would expect much more negative values of $\Delta S^{\neq}$ and lower values of $\Delta H^{\neq}$. The $\Delta H^{\neq}$ values are close to the Mo–CO bond dissociation energy [11] (approximately 30 kcal mol^{-1}), suggesting that the chelating effect does not play a significant role in these reactions.

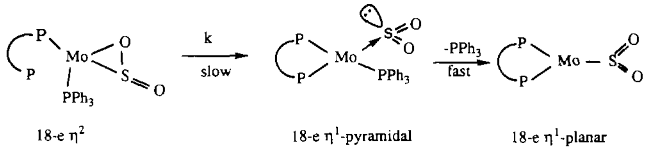
Table 1
Rate constants and activation parameters for PPh_3 substitution of $Mo(CO)_2(\eta^1\text{-L})(PPh_3)_2(SO_2)$ THF (Eq. (3)).

L	*T* (°C)	10^4 k (s^{-1})	$\Delta H^{\neq}$, (kcal mol^{-1})	$\Delta S^{\neq}$, (cal mol^{-1} K)
dmpe	4.5	3.06		
	15.0	7.26		
	26.0	16.3		
	26.0	15.6 [a]	12.3 ± 0.3	−30.3 ± 0.8
dppe	15.5	3.48		
	26.8	10.7		
	36.0	25.6	16.7 ± 0.2	−16.4 ± 0.6

[a] In the presence of excess of PPh_3 (0.14 M).

By comparison, the reaction of the corresponding molybdenum compounds used in our studies do show negative $\Delta S^{\neq}$ values and low $\Delta H^{\neq}$ values (Table I), consistent with an associative nucleophilic displacement process. When the difference between the two compounds $Mo(CO)_5(\eta^1\text{-L})$ and $Mo(CO)_2(\eta^1\text{-L})(PPh_3)_2(SO_2)$ is considered it is seen that three of the COs of the pentacarbonyl are replaced by two PPh_3 and one SO_2. Since CO is a strong π-acid, and since PPh_3 and SO_2 are stronger bases than CO, it follows that the electron density on Mo would be much higher in the compound used with the present study than in the pentacarbonyl. Also, it is clear that Mo in the present compound would be much more sterically hindered than in the pentacarbonyl.

Both the higher electron density on Mo and its steric crowding would tend to retard nucleophilic attack on Mo, yet the kinetic data (Table I) suggest otherwise. Since the results of the pentacarbonyl study [10] suggest chelate ring closure is not responsible for an associative pathway, one is prompted to define the role of SO_2 as a ligand that allows operation of an $\eta^2 \dashrightarrow \eta^1$-pyramidal$\dashrightarrow \eta^1$-planar reaction mechanism via an 18-electron intermediate or transition state (Scheme 1). Additional investigations are under way to further



(2 COs and 1 PPh_3 not shown)

Scheme 1.

examine the role of SO_2 as a ligand in substitution reactions of its metal complexes.

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[8] Preparation of $Mo(CO)_2(dmpe)(PPh_3)(SO_2)$: 350 mg of Mo $(CO)_2(PPh)_3(SO_2)(NCMe)$ [7] in 10 ml THF was mixed with 150 mg of dmpe ($C_2H_4(PMe_2)_2$) at 0°C. The solution was stirred for 2 h. The solvent was reduced to 2–3 ml under reduced pressure. 10 ml of toluene was added through a syringe and the solution was cooled to −20°C. The product was obtained as an orange powder (150 mg, yield = 53%). Deep red crystals were obtained from a CH_2Cl_2-toluene-pentane mixed solvent. H NMR (CD_2Cl_2): 0.83 (d, 6H); 1.75 (d, 6H); 1.2–1.8 (m, 4H); 7.4 (m, 9H); 7.6–7.7 (m, 6H). IR (CH_2Cl_2, cm^{-1}) ν_{CO}: 1869. νSO_2: 1188, 1053. Anal. Calc. for $C_{25}H_{31}MoO_4P_3S_1$: C, 49.69; H, 4.94. Found: C, 49.37; H, 4.88%. The analogous complex $Mo(CO)_2(dppe)(PPh_3)(SO_2)$ was made using the same method. IR (cm^{-1}) ν_{CO}: 1880 in THF; νSO_2: 1198, 1058 in CH_2Cl_2.

[9] Rate constants were obtained by following the decrease of the CO-stretching band of the reactant, using $\ln(A_t - A_\infty) = k_{obsd}t$ + constant. Plots of $\ln(A_t - A_\infty)$ vs. t were linear over two half lives ($r^2 > 0.995$). The reactants $Mo(CO)_2(\eta^1\text{-L})(PPh_3)_2(SO_2)$ were generated in situ by mixing the solution of $Mo(CO)_2$-$(PPh)_3(SO_2)(NCMe)$ with those of the ligands at −78°C. IR ν_{CO} for $Mo(CO)_2(\eta^1\text{-dppe})(PPh_3)_2(SO_2)$ in THF: 1937, 1876 cm^{-1}. IR ν_{CO} for $Mo(CO)_2(\eta^1\text{-dmpe})(PPh_3)_2(SO_2)$ in THF: 1934, 1867 cm^{-1}. The infrared spectra were obtained on a Nicolet 5PC-FTIR spectrophotometer equipped with a P/N 20.500 variable temperature IR cell witb 0.6 mm AgCl windows. Constant temperatures were obtained using a Neslab RTE-8 refrigeration circulating bath.

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