Supplementary Material Available: Listings of MNDO geometry optimized structures of all molecules and transition states shown in Figure 2 (8 pages). Ordering information is given on any current masthead page.

Notes

Contribution from the Department of Chemistry,
Auburn University, Auburn, Alabama 36849,
and Department of Natural Science,
Eastern Montana College, Billings, Montana 59101

Interaction of Complexes $Mn(PPhMe_2)Br_2$ and $Mn(PEt_3)Br_2$ with Sulfur Dioxide

W. E. Hill,[*†] S. D. Worley,[*†] D. K. Paul,[†] and V. F. Newberry[‡]

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There has been considerable recent interest in complexes of the form $MnLX_2$ (L = tertiary phosphine, X = anion) and their interaction with dioxygen.[1,2] Infrared work in these laboratories concerning films of the complexes has shown that the complexes do exist and that some do interact reversibly with dioxygen, the extent of which is markedly dependent upon the nature of the tertiary phosphine ligand.[3,4] All of the complexes studied here, however, exhibit competing irreversible decay channels at room temperature to the corresponding phosphine oxide complexes.[3,4] The purpose of this note is to report infrared data concerning the interaction of the complex films with sulfur dioxide.

The complex films studied here were prepared by sublimation of $MnBr_2$ onto a KBr infrared window followed by heating to ca. 473 K in a specially designed infrared cell[3,4] at 10^{-6} torr to remove all water. Then the dry $MnBr_2$ films were exposed to either $PPhMe_2$ or PEt_3 in situ to form the $MnLX_2$ complex films. Extensive evacuation at 10^{-6} torr was employed to remove all traces of excess phosphine. The films thus prepared were exposed to SO_2/evacuation cycles with infrared spectra (Perkin-Elmer Model 580 or 983 instrument with data station) being monitored at appropriate intervals. Since $SO_2(g)$ exhibits infrared bands near 520, 1150, and 1360 cm^{-1}, which might have interfered with resolution of the complex bands, the cell was always briefly evacuated following SO_2 exposure immediately before infrared analysis.

Figure 1 shows the infrared spectra corresponding to the $Mn(PPhMe_2)Br_2$ complex film interacting with SO_2. A comparison of Figure 1, parts b and a, reveals that new infrared bands at (SO_2 ($S^{18}O_2$)) 412 (410), 445 (440), 525 (515), 785 (780), 995 (950), 1002 (968), and 1075 (1028) cm^{-1} appear that can be attributed to a new complex(es) formed from the reaction of SO_2 with $Mn(PPhMe_2)Br_2$. The intense band at 1115 cm^{-1} in Figure 1b, which does not shift appreciably upon $S^{18}O_2$ exposure, can be assigned to a ligand vibrational mode ($\nu_{PC\text{-aryl}}$), which is accentuated due to the presence of SO_2; this band was also observed to be enhanced by the presence of dioxygen.[4] All of the bands mentioned above declined markedly upon evacuation at 10^{-6} torr for 12 h (Figure 1c). We have been able to observe cycling of the intensities of these bands upon reexposure/evacuation for up to three cycles; ca. 12-h evacuation is required to essentially remove the SO_2. However, upon lengthy exposure (72 h) at high pressure (120 torr) the spectrum shown in Figure 1d resulted, which could not be reversed by lengthy evacuation. The bands at 995, 1002, and 1075 cm^{-1} for the complex shift substantially when $S^{18}O_2$ is used and obviously correspond to S–O stretching vibrational modes; the fact that three such bands were present indicates that more than one type of complex is probably being formed. On the other hand, the bands at 412 and 445 cm^{-1} shifted little upon isotopic substitution; these bands could correspond to Mn–S modes. The bands at 525 cm^{-1} in Figure 1b and 625 cm^{-1} in Figure 1d did shift appreciably when $S^{18}O_2$ was employed and probably correspond to Mn–O modes.

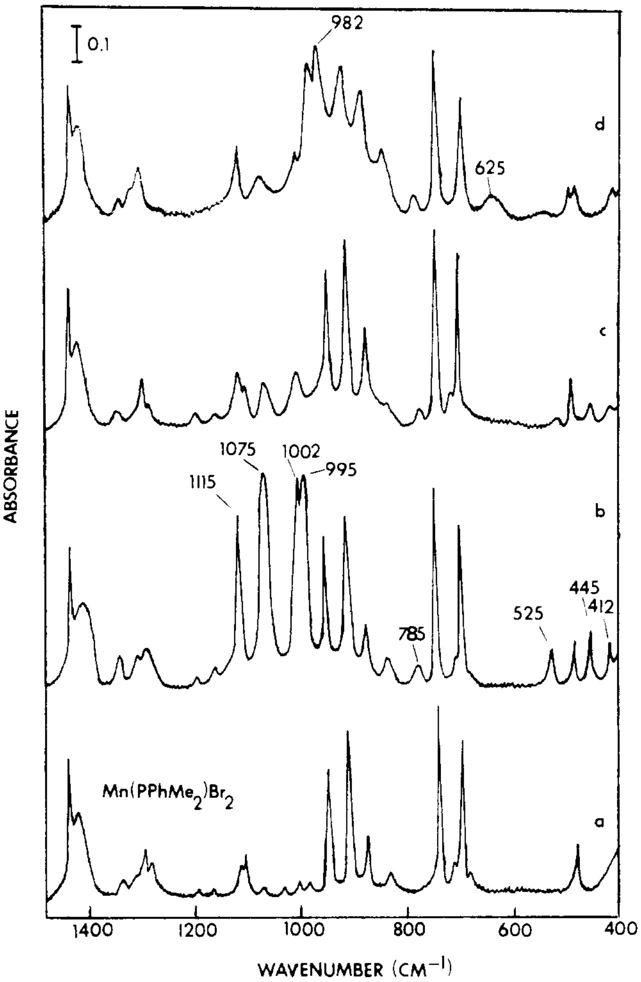

Figure 1. Infrared spectra of a $Mn(PPhMe_2)Br_2$ film: (a) following initial preparation; (b) following exposure to 50 torr of SO_2 for 24 h at 298 K and then brief evacuation; (c) following an evacuation cycle for 12 h at 10^{-6} torr at 298 K; (d) following exposure to 120 torr of SO_2 for 72 h at 298 K and lengthy evacuation.

Figure 2 shows a similar series of experiments for $Mn(PEt_3)Br_2$ interaction with SO_2. Band positions for $S^{18}O_2$ complex spectra

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[†] Auburn University.

[‡] Eastern Montana College.

(1) McAuliffe, C. A. *J. Organomet. Chem.* **1982**, *228*, 255 and numerous references quoted therein.

(2) Brown R. M.; Bull, R. E.; Green, M. L. H.; Grebenik, P. D.; Martin-Polo, J. J.; Mingos, D. M. P. *J. Organomet. Chem.* **1980**, *201*, 437.

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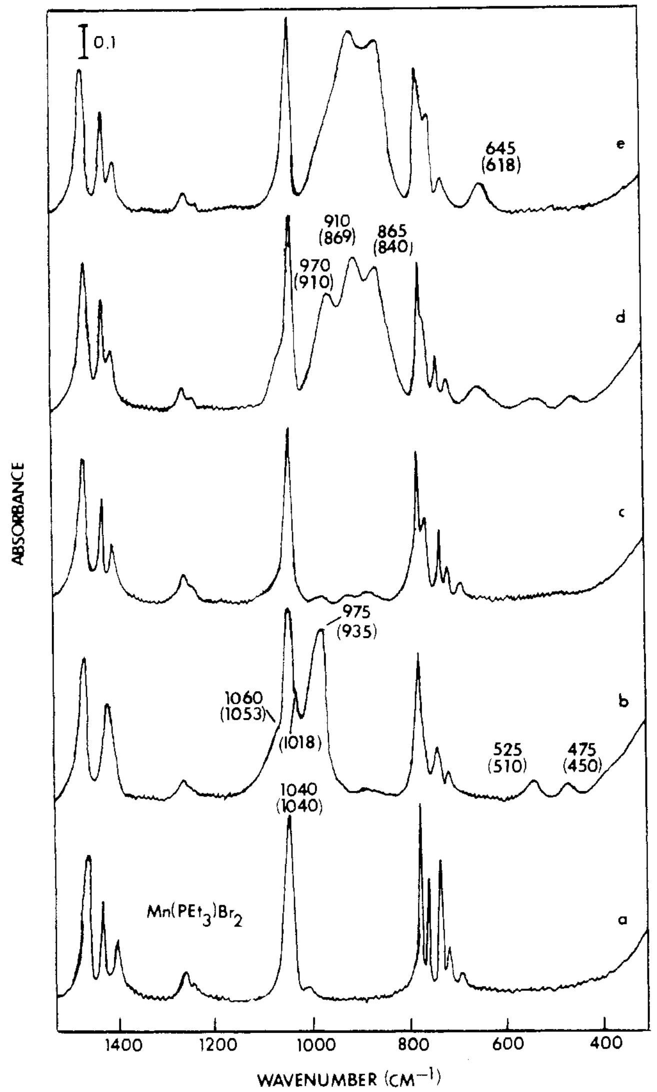

Figure 2. Infrared spectra of a Mn(PEt$_3$)Br$_2$ film: (a) following initial preparation; (b) following exposure to 15 torr of SO$_2$ for 15 min at 298 K and then brief evacuation; (c) following an evacuation cycle for 24 h at 10^{-6} torr at 298 K; (d) following exposure to 50 torr of SO$_2$ for 24 h at 298 K and then brief evacuation; (e) following evacuation for 24 h at 10^{-6} torr at 298 K. Band positions for analogous $S^{18}O_2$ complex spectra are given in parentheses.

are shown in parentheses. Again reversibility was observed as long as exposure time and pressure were minimized. It is clear that at least two types of $MnLBr_2/SO_2$ complexes were formed in these experiments—one in which the SO$_2$ bonds reversibly and one in which the SO$_2$ is coordinated in an irreversible fashion. Comparison of the intensities of the 865-, 910-, and 970-cm^{-1} bands in the spectra shown in Figure 2, parts d and e, reveals that the reversible complex can decompose to the irreversible one even during evacuation following high SO$_2$ exposures.

Bulk samples of the two final irreversible SO$_2$ complexes were prepared on a high-vacuum line in a manner completely analogous to the sample treatment conditions for the complex films. The bulk analyses of the two final irreversible SO$_2$ complexes revealed that the stoichiometry for each was $MnLBr_2\cdot{}^1/_2SO_2$.[5] This data along with the observation of intense infrared bands in the 800–1075-cm^{-1} regions of the spectra imply that the two forms of each complex contain SO$_2$ bonded in a bridging mode,[6] with more than one atom of SO$_2$ involved in the bridge. Final structure determination must await X-ray crystallographic data.

It should be noted that McAuliffe and co-workers have reported recently the reaction of SO$_2$ with several $MnLX_2$ complexes in toluene solution and in toluene slurries.[7] They report a stoichiometry of $MnLX_2\cdot{}^2/_3SO_2$ for their solution studies, and they were not able to observe reversibility. Furthermore, they report prominent infrared bands in the 1112–1140-cm^{-1} region, which are not observed for the $MnPEt_3Br_2/SO_2$ complex film. However, their experimental conditions (liquid phase, exposure to 760 torr of SO$_2$ for 48 h) were markedly different than those used in this work; thus it is possible that a reversible complex was formed also in their work, but converted to an irreversible product before analysis.

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Registry No. Mn(PPhMe$_2$)Br$_2$, 71957-10-3; Mn(PEt$_3$)Br$_2$, 82758-64-3; SO$_2$, 7446-09-5.

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(5) Anal. Calcd (Atlantic Microlabs, Inc.) for $Mn(PPhMe_2)Br_2\cdot{}^1/_2SO_2$: C, 25.0; H, 2.9; Br, 41.5; S, 4.2. Found: C, 24.8; H, 3.0; Br, 41.4; S, 4.1. Anal. Calcd (Atlantic Microlabs, Inc.) for $Mn(PEt_3)Br_2\cdot{}^1/_2SO_2$: C, 19.7; H, 4.1; Br, 43.8, S, 4.4. Found: C, 19.7; H, 4.2; Br, 43.7; S, 4.4.

(6) See for example: Vitzthum, G.; Lindner, E. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 315. Kubas, G. J. *Inorg. Chem.* **1979**, *18*, 182. Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding (Berlin)* **1981**, *46*, 47. Jarvinen, G. D.; Kubas, G. J.; Ryan, R. R. *J. Chem. Soc., Chem. Commun.* **1981**, 305. Briant, C. E.; Hughes, G. R.; Minshall, P. C.; Mingos, D. M. P. *J. Organoomet. Chem.* **1982**, *224*, C21. Briant, C. E.; Theobald, B. R. C.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 963.

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Contribution from the Laboratory for Inorganic Chemistry,
ETH-Zentrum, CH-8092 Zürich, Switzerland,
and Istituto di Chimica Farmaceutica,
University of Milan, I-20131 Milano, Italy

Platinum(II) Trichlorostannate Complexes with Nitrogen Ligands. ^{195}Pt, ^{119}Sn, ^{31}P, and ^{15}N NMR Studies and the X-ray Crystallographic Structure of (*p*-Chloroaniline)(triethylphosphine)chloro(trichlorostannato)platinum(II)

A. Albinati, H. Moriyama, H. Rüegger, P. S. Pregosin,* and A. Togni

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Although there are now many well-characterized SnCl$_3$ complexes of platinum(II),[1] these frequently contain phosphorus, arsenic, carbonyl, or halogen ligands. We were interested in obtaining platinum(II) trichlorostannate complexes with nitrogen ligands since the latter are readily available with optically active carbon centers. As complexes of platinum(II) with SnCl$_3$ ligands are active catalysts for the hydrogenation[2] and hydroformylation[3] reactions, introduction of an available optically active center might eventually afford a new optically active catalyst. Further, since there is little known concerning the trans influence of the SnCl$_3$ it would be useful to have crystallographic and NMR measurements on a relatively simple system, for comparison purposes. We report here the preparation and characterization of the complexes [PtCl(SnCl$_3$)L(PEt$_3$)], L = **1**–**3**, and the molecular structure for the complex with L = **1a** and suggest that all of these complexes have nitrogen coordinated to platinum.

Results

1. X-ray Structure of [PtCl(SnCl$_3$)(1a)(PEt$_3$)]. The complexes [PtCl(SnCl$_3$)L(PEt$_3$)] were prepared by reaction of 2 equiv of

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* To whom correspondence should be addressed at the ETH-Zentrum.