New Oxomolybdenum(V) Compounds of Tetraphenylporphine

Sir:

The importance of oxomolybdenum(V) compounds in a number of biochemical redox reactions[1] and in the development of theories of bonding in their coordination compounds[2] prompts us to report the synthesis and characterization of three new paramagnetic compounds of molybdenum with tetraphenylporphine (abbreviated subsequently as TPP).

The compound MoO(OH)TPP (I) was prepared by dissolving 1 g of TPP in 400 ml of decalin and adding 7 g of $Mo(CO)_6$. This mixture was refluxed on a hot plate in a nitrogen atmosphere for 5–6 hr.[3] The solution was cooled and passed through a column packed with dry activated alumina. The column was first eluted with benzene and later with chloroform. The fraction of benzene and the first fraction of chloroform were discarded. The final green fraction was concentrated in the Vapsilator under reduced pressure. The concentrated solution was mixed with a few milliliters of xylene and kept several days for crystallization. The crystals obtained were filtered, washed with cold xylene, and dried in air. Finally, the crystals were dried *in vacuo* at 100° (0.25 g). *Anal.* Calcd for MoO(OH)TPP, $C_{44}H_{29}N_4O_2Mo$: C, 71.26; H, 3.91; N, 7.56. Found: C, 71.30; H, 3.78; N, 7.36. The ir spectrum of I showed five additional bands in the region 4000–550 cm^{-1} as compared to the TPP spectrum, and these bands are 902 (m), 887 (w), 648 (vs), 614 (vs), and 567 (s) cm^{-1}. These bands are probably associated with molybdenum–oxygen vibrations. The bands at 3350, N–H stretch, and 698 cm^{-1}, out-of-plane N–H deformation,[4] of TPP free base are missing in I and the other two compounds described below. The visible absorption spectrum of I in benzene has peaks at 408, 446, 585, 615, and 667 nm with extinction coefficients of 38×10^3, 58.5×10^3, 4.3×10^3, 5.2×10^3, and 3.9×10^3 M^{-1} cm^{-1}, respectively.[5]

The second compound, MoO(Cl)TPP (II), was prepared by stirring a chloroform solution of 0.25 g of I with a few milliliters of concentrated hydrochloric acid for 3–4 hr. The final solution was concentrated to dryness in the Vapsilator under reduced pressure. The solid obtained was dissolved in chloroform containing a few milliliters of xylene and concentrated to a small volume. The concentrated solution was kept for crystallization. The crystals (0.2 g) obtained were filtered, washed with cold xylene, and finally dried *in vacuo* at 100° for several hours. *Anal.* Calcd for MoO(Cl)TPP·HCl, $C_{44}H_{29}N_4OCl_2Mo$: C, 66.33; H, 3.64; N, 7.04; Cl, 8.92. Found: C, 66.94; H, 3.62; N, 6.76; Cl, 8.40. The ir spectrum of II showed an additional band as compared to TPP (free base), and it was at 941 (Mo=O stretch). The visible spectrum of MoO(Cl)TPP·HCl in chloroform has peaks at 382, 420, 448, 504, 631, and 676 nm with extinction coefficients of 41.5×10^3, 32.0×10^3, 27.0×10^3, 44×10^3, 8.9×10^3, and 9.45×10^3, respectively.

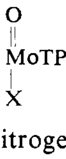
The third compound, MoO(OOH)TPP (III), was prepared by dissolving 0.25 g of II in benzene and chromatographing the benzene solution on a column packed with dry activated alumina. The column was first eluted with benzene and later with a 1:1 mixture of benzene and chloroform. The later fraction was concentrated under reduced pressure and the solution was kept for crystallization. The crystals (0.2 g) obtained were filtered, washed with cold benzene, and dried in air. *Anal.* Calcd for MoO(OOH)TPP, $C_{44}H_{29}N_4O_3Mo$: C, 69.75; H, 3.83; N, 7.40. Found: C, 69.81; H, 3.94; N, 6.99. The main difference in the ir spectra of III and free TPP is six additional bands in the former compound. The bands are at 1146 (shoulder), 1132 (s), 900 (vs), 648 (vs), 615 (vs), and 564 (s) cm^{-1}. These bands are associated with molybdenum–oxygen and O–O vibrations.[6] The visible absorption spectrum of III in benzene has peaks at 411, 445, 556, 584, 616, 640 (shoulder), and 664 nm with extinction coefficients of 41.5×10^3, 59.0×10^3, 4.7×10^3, 5.9×10^3, 4.6×10^3, and 4.4×10^3, respectively. Compound III can be transformed into II by adding concentrated hydrochloric acid to a solution of the former compound in benzene. Compounds I and II react with strong bases such as pyridine[7] to form new species.

The magnetic susceptibility of I, II, and III was determined by the Faraday method using $HgCo(NCS)_4$ as a standard. The following values of the effective magnetic moment[8] were determined: for MoO(OH)TPP μ_{eff} = 1.75 (294°K), 1.74 (203°K), and 1.70 (79°K); for MoO(Cl)TPP μ_{eff} = 1.74 (294°K) and 1.68 (79°K); and for MoO(OOH)TPP μ_{eff} = 1.76 (294°K) and 1.72 (79°K). This indicates that molybdenum in these compounds has a spin of $^1/_2$ and is in a 5+ oxidation state.

The room-temperature esr spectra of I and III in benzene and II in chloroform were measured on the Varian E3 esr spectrometer and the esr parameters are as follows.

Species	*g*	*A*,[9] G
MoO(OH)TPP in C_6H_6	1.987 ± 0.001	50
MoO(OOH)TPP in C_6H_6	1.983 ± 0.001	50
MoO(Cl)TPP·HCl in CH_3Cl	1.983 ± 0.001	50

This again confirms the d^1 configuration in the above compounds. Thus these compounds can be formulated as



$$\begin{array}{l} \mathrm{O} \\ \| \\ \mathrm{MoTPP} \\ | \\ \mathrm{X} \end{array}$$

where the four pyrrole nitrogens of the TPP and molyb-

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[1] J. T. Spence, *Coord. Chem. Rev.*, **4**, 475 (1968).

[2] P. C. H. Mitchell, *Quart. Rev., Chem. Soc.*, **20**, 103 (1966).

[3] It is not clear to us what the oxidizing agent is in these reactions. The most likely possibility is the solvent, which has some reduced impurities in it. The ligand itself could also be involved in the oxidation reaction.

[4] D. Thomas and A. Martell, *J. Amer. Chem. Soc.*, **78**, 1338 (1956).

[5] The solubility of these molybdenum porphyrins was too low to accurately determine their molecular weights in solution.

[6] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **91**, 55 (1969).

[7] MoO(OH)TPP dissolves in pyridine and gives an absorption spectrum with maxima at 402 (sh), 421, 448, 554 (sh), 582, 619, and 647 nm with extinction coefficients 25×10^3, 59×10^3, 89×10^3, 4.1×10^3, 6.65×10^3, 6.15×10^3, and 3.8×10^3, respectively, whereas MoO(OOH)TPP dissolved in pyridine gives an absorption spectrum with maxima at 402 (sh), 421, 449, 548, 590, 614, and 653 nm with extinction coefficients 26.5×10^3, 60×10^3, 88×10^3, 5.3×10^3, 8.15×10^3, and 6.7×10^3, respectively.

[8] $\mu_{eff} = 2.83\sqrt{\chi_M T}$ BM, where χ_M has been corrected for a diamagnetic correction of the TPP of 370×10^{-6} cgs. The μ_{eff}'s are in units of Bohr Magnetons.

[9] *A* is the value of hyperfine splitting due to the $^5/_2$ spin of the ^{95}Mo and ^{97}Mo nuclei.

denum are nearly in a plane, and oxygen and X groups (X = OH, OOH, Cl) occupy axial positions.

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Mechanism of Oxidative Addition Reactions. Retention of Configuration in the Reaction of Alkyl Halides

Sir:

There is great current interest in the mechanism(s) of oxidative addition of molecules XY to square-planar d^8 complexes.[1] We have made several observations which give detailed information for the reaction of Ir(CO)ZL$_2$ (Z = Cl, I, SCN; L = P(C$_6$H$_5$)$_3$, P(C$_6$H$_5$)$_2$CH$_3$) with certain alkyl halides.

We conclude (1) that these reactions occur in a one-step, concerted process without the formation of intermediates, and in the absence of solvents; (2) that retention of configuration results at the carbon center of the alkyl group; and (3) a trans addition with respect to the square plane can occur even with these restrictions.

These results are in agreement with the predictions made on the basis of orbital symmetry arguments[2] (Figure 1a and b). The iridium complexes used are well known to act as nucleophiles, or as Lewis bases, in their reactions.[3] The highest filled molecular orbitals are chiefly d orbitals of the metal.

The compounds Ir(CO)(SCN)L$_2$ were made from Ir(CO)ClL$_2$[4] by addition of [(C$_4$H$_9$)$_4$N]SCN in dichloroethane solution and precipitated with methanol. CH$_3$SCN and CH$_3$Cl react very slowly at room temperature with these complexes. Mixing Ir(CO)(SCN)L$_2$ with CH$_3$I in the presence of a very large excess of SCN$^-$ in dichloroethane solution yields only Ir(CO)(SCN)L$_2$(CH$_3$)I. Similarly, Ir(CO)ClL$_2$, upon addition of CH$_3$I with excess Cl$^-$, gives only Ir(CO)ClL$_2$(CH$_3$)I. The Ir(CO)ClL$_2$(CH$_3$)Cl species are stable compounds and inert toward I$^-$ substitutions on this time scale. These products were precipitated from solution with methanol and recrystallized for analysis from benzene-methanol. Infrared and nmr spectra of the products in solution prior to and after recrystallization were identical.

Solid Ir(CO)ClL$_2$ compounds were both found to react readily with CH$_3$I gas at room temperature. Similarly, the more reactive Ir(CO)Cl[P(C$_6$H$_5$)$_2$CH$_3$]$_2$ adds CH$_3$Br gas. Infrared and far-infrared analyses of these products show they are identical with those found in solution. The product of CH$_3$Br addition has been shown by analysis of far-infrared Ir–Cl stretching frequency and nmr to be the result of trans addition.[5] By a similar analysis, the stereochemistry of both the products of CH$_3$I addition was also found to be the result of trans addition ($\nu_{\mathrm{Ir-Cl}} = 300$ cm^{-1} for both products).

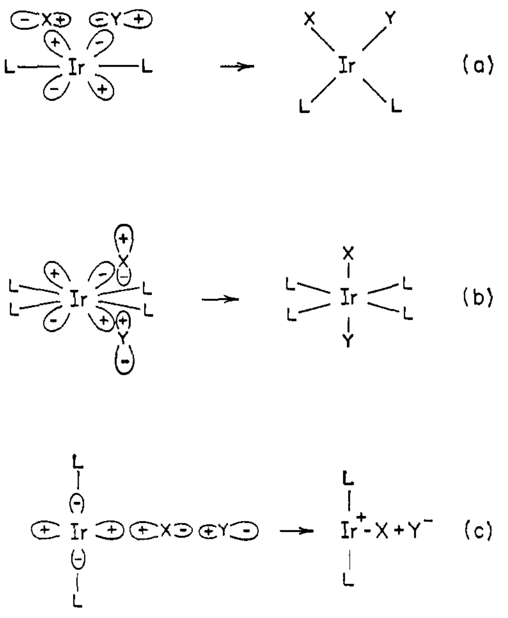

Figure 1. (a) One-step cis addition; retention of configuration at X. (b) One-step trans addition; retention at X. (c) Two-step cis or trans addition; inversion at X.

Optically active CH$_3$CHBrCOOC$_2$H$_5$ ($[\alpha]^{25}\mathrm{D}$ $-6.0°$) was obtained by resolution of CH$_3$CHBrCOOH[6] and conversion to the ester in HBr saturated ethanol. Ir(CO)Cl[P(C$_6$H$_5$)$_2$CH$_3$]$_2$ was stirred at room temperature with an equimolar amount of the ester in dichloromethane solution. The progress of the reaction was followed by the disappearance of the infrared carboxyl stretch of the free ester at 1742 cm^{-1} and the appearance of the coordinated ester carboxyl peak at 1698 cm^{-1}. After 4 days the solvent was evaporated and any remaining unreacted ester removed by repeated washings with pentane and pumping on the solid for 24 hr with a mercury diffusion pump. The product, Ir(CO)Cl[P(C$_6$H$_5$)$_2$CH$_3$]$_2$(CH$_3$CHCO$_2$C$_2$H$_5$)Br, was found to be optically active, $[\alpha]^{25}\mathrm{D} \sim -20°$. This complex was treated by slow addition of an equimolar amount of Br$_2$ in THF at $-78°$ for 24 hr. An infrared spectrum of the product showed greater than 95% cleavage of the alkyl–metal bond to regenerate CH$_3$CHBrCOOC$_2$H$_5$. This ester in solution was removed from any remaining uncleaved complex by vacuum distillation. A rotation of $[\alpha]^{25}\mathrm{D} \sim -4°$ was measured for this product.

Since no halide ions in solution are incorporated into the product, a one-step addition is indicated. The reaction of Ir(CO)Cl[P(C$_6$H$_5$)$_3$]$_2$ with CH$_3$I in the presence of ^{131}I$^-$ is also known to show no ^{131}I in the product.[7] One-step addition is further indicated by

(1) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **88**, 3511 (1966); A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1562 (1969); I. C. Donek and G. Wilkinson, *ibid.*, *A*, 2604 (1969); J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

(2) L. Salem, *Chem. Brit.*, 449 (1969); R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970).

(3) D. F. Shriver, R. N. Scott, and D. Lehman, *Inorg. Chim. Acta*, **4**, 73 (1970).

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