

chemistry of more electron-rich iron dihydride complexes is currently being studied.

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Synthesis and Characterization of $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$ ($\text{R} = \text{C}_2\text{H}_5$ or C_3H_7): Distinction between Phosphines and Phosphonium Ions Using Secondary Ion Mass Spectrometry

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The reaction between the dinuclear quadruply bonded $\text{Mo}_2(\text{mhp})_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine) and gaseous hydrogen chloride in ethanol in the presence of the tertiary phosphines PEt_3 or *P-n-Pr*₃ affords the (μ -hydrido)-dimolybdenum(III) complexes $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$. The characterization of these complexes has included measurement of their secondary ion mass spectra (SIMS). A study of the SIMS spectra of complexes of molybdenum and rhenium that contain trialkylphosphine ligands has shown that it is possible to differentiate between phosphonium ions $([\text{R}_3\text{PH}]^+)$ and neutral PR_3 ligands in these complexes. Such a distinction did not exist between complexes containing the analogous $(\text{Ph}_3\text{PH})^+$ and PPh_3 moieties.

Introduction

The technique of secondary ion mass spectrometry (SIMS) has found application in the analysis of surface structure of catalytic importance. Its recent utilization in the study of organic,^{1,2} biological,^{3,4} inorganic,⁵⁻⁷ and organometallic⁷ complexes has also demonstrated the potential of SIMS for the analysis of molecular species. Structural information of nonvolatile species is attainable from such studies via the appearance of molecular species M^+ and cationized adducts such as $[\text{M} + \text{H}]^+$ and $[\text{M} + \text{C}]^+$, where the cationizing agent C is often an alkali-metal additive or Ag from the silver support typically employed in such analyses. This technique complements field desorption mass spectrometry⁸ as a means of mass analyzing nonvolatile samples and is suited to the characterization of inorganic and organometallic species as recently demonstrated.^{7,9} The present study arose out of our spectroscopic characterization of the products that emanate from the reaction between the quadruply bonded dimolybdenum complex $\text{Mo}_2(\text{mhp})_4$, where mhp represents the anion of 2-hydroxy-6-methylpyridine, and gaseous hydrogen chloride in the presence of tertiary phosphines.¹⁰⁻¹² The question that was posed to us during this investigation concerned the use of SIMS to differentiate phosphonium ions

$([\text{R}_3\text{PH}]^+)$ from neutral phosphine ligands (PR_3) in complexes that might be difficult to analyze by conventional techniques. Since the direct sputtering of cations is an ionization process of high efficiency in the SIMS experiment,¹³ we were particularly interested in whether large relative differences in the $[\text{R}_3\text{PH}]^+$ ion abundances could be used to distinguish between cationic and neutral phosphine species in transition-metal complexes. The possibility of using SIMS to identify transition-metal phosphines is of additional note since it could conceivably provide a means of characterizing heterogenized homogeneous catalysts derived from complexes containing phosphine ligands. Drawing upon complexes prepared for the first time in the present work, together with various phosphine complexes of molybdenum and rhenium that were already available in our laboratory from previous studies, we have carried out such an investigation and herein describe the pertinent details.

Experimental Section

Materials. Hydrogen chloride gas was purchased from Matheson and used without further drying. Alkylphosphines were purchased from Strem Chemicals. The following compounds were prepared according to literature procedures: $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$, where $\text{R} = \text{Et}$, *n-Pr*, or *n-Bu*,¹⁴ $\text{MoCl}_4(\text{PEtPh}_2)_2$,¹⁵ $\text{MoCl}_4(\text{P}^i\text{Pr}_2)_2$,¹⁵ $[\text{Mo}(\text{CNCMe}_3)_6(\text{PEt}_3)](\text{PF}_6)_2$,¹⁶ $\text{Mo}_2(\text{mhp})_4$,¹⁷ where mhp is the anion of 2-hydroxy-6-methylpyridine, $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$, where $\text{R} = \text{Et}$ or Ph ,¹⁸ $\text{ReCl}_3(\text{PMe}_2\text{Ph})_3$,¹⁹ $\text{ReOCl}_3(\text{PPh}_3)_2$,²⁰ $\text{Re}_2\text{H}_8(\text{PPh}_3)_4$,²¹ $\text{ReH}_3(\text{PPh}_3)_3$, $\text{ReH}_3(\text{PPh}_3)_2(\text{PEt}_2\text{Ph})$, and $\text{ReH}_3(\text{PPh}_3)_2\text{py}$.²²

Reaction Procedures. All reactions were carried out under a nitrogen atmosphere, and all solvents were dried and deoxygenated prior to use by purging with N_2 gas.

- (1) Liu, L.; Unger, S. E.; Cooks, R. G. *Tetrahedron* **1981**, *37*, 1067.
- (2) Benninghoven, A.; Jaspers, D.; Sichtermann, W. *Appl. Phys.* **1976**, *11*, 35.
- (3) Liu, L.; Busch, K. L.; Cooks, R. G. *Anal. Chem.* **1981**, *53*, 109.
- (4) Benninghoven, A.; Sichtermann, W. *Anal. Chem.* **1978**, *50*, 1180.
- (5) Honda, F.; Lancaster, G. M.; Fukuda, Y.; Rabalais, J. W. *J. Chem. Phys.* **1978**, *69*, 4931.
- (6) Ganjei, J. D.; Colton, R. J.; Murday, J. S. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *37*, 49.
- (7) Pierce, J.; Busch, K. L.; Walton, R. A.; Cooks, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2583.
- (8) See, for example: Games, D. E.; Gower, J. L.; Kane-Maguire, L. A. *P. J. Chem. Soc., Dalton Trans.* **1981**, 1994. Henis, N. B. H.; Lamanna, W.; Humphrey, M. B.; Bursey, M. M.; Brookhart, M. S. *Inorg. Chim. Acta* **1981**, *54*, L11.
- (9) Pierce, J. L.; Busch, K. L.; Cooks, R. G.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 2597.
- (10) Analogous studies involving the reaction between $\text{W}_2(\text{mhp})_4$ and gaseous hydrogen chloride have been published elsewhere.^{11,12}
- (11) DeMarco, D.; Nimry, T.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 575.
- (12) Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Fang, A.; Ilisley, W. H.; Kolthammer, B. W. S.; Walton, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 5078.

- (13) Day, R. J.; Unger, S. E.; Cooks, R. G. *Anal. Chem.* **1980**, *52*, 557A.
- (14) Glicksman, H. D.; Hamer, A. D.; Smith, T. S.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205.
- (15) Pennella, F. *Inorg. Synth.* **1974**, *15*, 43.
- (16) Brant, P.; Cotton, F. A.; Sekutowski, J. C.; Wood, T. E.; Walton, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 6588.
- (17) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. *J. Am. Chem. Soc.* **1978**, *100*, 4725.
- (18) Cotton, F. A.; Foxman, B. M. *Inorg. Chem.* **1968**, *7*, 2135.
- (19) Parshall, G. W. *Inorg. Synth.* **1977**, *17*, 111.
- (20) Reference 19, p 110.
- (21) Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2674.
- (22) Chatt, J.; Coffey, R. S. *J. Chem. Soc. A* **1969**, 1963.

A. Reactions of $\text{Mo}_2(\text{mhp})_4$ with Gaseous Hydrogen Chloride. (i) $(\text{Et}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$. A quantity of $\text{Mo}_2(\text{mhp})_4$ (1.0 g, 1.6 mmol) was suspended in 35 mL of ethanol. A stream of hydrogen chloride gas was introduced and bubbled through the solution, and triethylphosphine (0.7 mL, 4.7 mmol) was syringed into the reaction mixture. The addition of hydrogen chloride was continued until a yellow color appeared and all of the starting material had reacted. The resulting mixture was filtered and stripped to dryness under reduced pressure. The product was extracted into CH_3CN , leaving behind 0.55 g of insoluble $(\text{mhpH}_2)\text{Cl}$. The CH_3CN extract was filtered, and isopropyl alcohol was added dropwise to the filtrate to induce the precipitation of 0.55 g of the gold-colored crystalline product, yield 41%. Anal. Calcd for $\text{C}_{18}\text{H}_{48}\text{Cl}_8\text{Mo}_2\text{P}_3$: C, 25.94; H, 5.76; Cl, 34.06. Found: C, 26.00; H, 5.73; Cl, 33.76.

(ii) $(n\text{-Pr}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$. This complex was prepared in 26% yield by a procedure similar to that described in section i. Anal. Calcd for $\text{C}_{27}\text{H}_{67}\text{Cl}_8\text{Mo}_2\text{P}_3$: C, 33.49; H, 6.93; Cl, 29.31. Found: C, 33.75; H, 6.95; Cl, 29.51.

B. Preparation of Phosphonium Salts of the $[\text{Re}_2\text{Cl}_8]^{2-}$ Anion. (i) $(\text{Et}_3\text{PH})_2\text{Re}_2\text{Cl}_8$. A quantity of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ (0.5 g, 0.43 mmol) was placed in a round-bottom flask equipped with a reflux condenser that contained 20 mL of a 2:1 mixture of concentrated HCl and methanol. The resulting solution was refluxed for 10 min and the hot solution filtered into a mixture of concentrated HCl (20 mL) and PEt_3 (1.0 mL, 6.77 mmol). The blue-green product precipitated upon cooling; yield 28%.

(ii) $(\text{Ph}_3\text{PH})_2\text{Re}_2\text{Cl}_8$. A mixture of $\text{Re}_2\text{Cl}_8(\text{PPh}_3)_2$ (0.2 g, 0.18 mmol) and PPh_3 (0.1 g, 0.38 mmol) was treated with 30 mL of concentrated HCl that had been saturated with HCl(g). This was refluxed for 5 min and then allowed to cool. The resulting blue-green solid was filtered off and washed with concentrated HCl (5 mL) followed by diethyl ether (30 mL); yield 90–95%.

C. Preparation of $\text{ReCl}_4(\text{P-}n\text{-Pr}_3)_2$. To the green-brown ethanol filtrate (10 mL) resulting from the synthesis of 1.26 g of $\text{Re}_2\text{Cl}_8(\text{P-}n\text{-Pr}_3)_4$ according to the procedure of Ebner and Walton²³ was added 10 mL of 6 N HCl. A yellow precipitate formed instantly upon addition of the HCl, but this disappeared upon refluxing the mixture. After 1 h of reflux, a purple solid (0.2 g) was filtered off and dried in vacuo. This product was identified as *trans*- $\text{ReCl}_4(\text{P-}n\text{-Pr}_3)_2$. Anal. Calcd for $\text{C}_{18}\text{H}_{42}\text{Cl}_4\text{P}_2\text{Re}$: C, 33.33; H, 6.48. Found: C, 33.52; H, 6.31.

Physical Measurements. SIMS spectra were obtained on a commercial Riber instrument (Model SQ 156L) in the positive-ion mode using an energy selector, a quadrupole mass filter, a Channeltron electron multiplier, and pulse-counting electronics. A 4-keV argon ion beam was used, and ion currents were typically held to 1×10^{-10} A/mm². Chamber pressure was on the order of 1×10^{-8} torr or less. Samples were burnished onto an abrasively cleaned 1-cm² silver foil. In the derivatization experiments, *p*-toluenesulfonic acid (*p*-TSA) was dissolved in ethanol and a drop was added directly to the sample supported on the foil.

In the case of the characterization of the new complexes $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$ (R = Et or *n*-Pr), infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded on dichloromethane solutions with use of a Varian Series 634 spectrophotometer. Nuclear magnetic resonance spectra were recorded, in acetonitrile-*d*₃ with tetramethylsilane (Me_4Si) as an internal reference, with use of a Perkin-Elmer R-32 90-MHz NMR spectrometer. A Hewlett-Packard Model 5950A ESCA spectrometer was used to record the X-ray photoelectron spectra with use of the procedure described previously.²⁴ Electrochemical measurements were made on dichloromethane or acetonitrile solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Potentials are referenced to the saturated potassium chloride calomel electrode (SCE) at 22 ± 2 °C and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed with a Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder.

Results and Discussion

(a) Preparation of $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$ and Preliminary Characterization Studies.

(23) Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987.

(24) Mialki, W. S.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 2791.

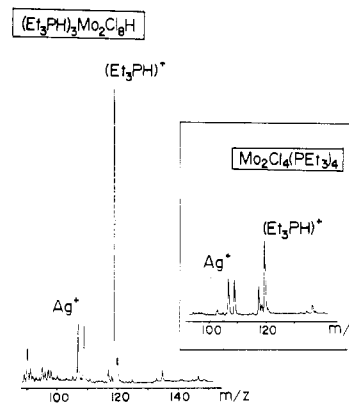


Figure 1. SIMS spectra of $(\text{Et}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$ vs. $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$ comparing intensities of the $[\text{Et}_3\text{PH}]^+$ ion.

represents the anion of 2-hydroxy-6-methylpyridine) with gaseous hydrogen chloride in the presence of PEt_3 or *P-n*- Pr_3 in alcohol solvents affords the doubly bonded ditungsten(IV) species $\text{W}_2\text{Cl}_4(\text{OR})_4(\text{ROH})_2$.^{11,12} In contrast to this, it is found that the analogous room-temperature reaction involving $\text{Mo}_2(\text{mhp})_4$ gives the (μ -hydrido)dimolybdenum(III) species $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$. This result is in accord with (1) the expectation that a low-oxidation-state complex of a third-row element such as tungsten is more susceptible to oxidation than its second-row congener and (2) previous observations^{25,26} that quadruply bonded $\text{Mo}_2(\text{O}_2\text{CR})_4$ compounds react with concentrated HCl to afford $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$ at temperatures of 60 °C and above. A noteworthy feature of the triethylphosphonium and tri-*n*-propylphosphonium salts prepared in the present study was their much greater solubility in nonaqueous solvents compared to such properties of the alkali-metal²⁵ and pyridinium salts.²⁶ This has permitted for the first time an adequate spectroscopic characterization of $[\text{Mo}_2\text{Cl}_8\text{H}]^{3-}$ in nonaqueous media. The pertinent spectroscopic properties of the solid salts and their dichloromethane or acetonitrile solutions are summarized in ref 27. The infrared, electronic absorption, and X-ray photoelectron spectra of $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$ are in good agreement with literature data for the alkali-metal salts of this anion.^{25,28–31} The most interesting features in the ¹H NMR spectra (in CD_3CN) of

(25) Cotton, F. A.; Kalbacher, B. J. *Inorg. Chem.* **1976**, *15*, 522.

(26) Bino, A.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 332.

(27) The spectroscopic properties of $(\text{Et}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$ are summarized here. Those of the tri-*n*-propylphosphonium salt are very similar and details are available from R.A.W. upon request. (i) XPS Mo $3d_{3/2,5/2}$ binding energies of the solid: 232.7 and 229.5 eV. (ii) IR (Nujol mull): 2428 w [$\nu(\text{P-H})$], 1620 w [$\nu(\text{MoHMo})$ sym], 1275 m-w [$\nu(\text{MoHMo})$ asym] cm^{-1} . IR (CH_2Cl_2): 2424 w, 1612 w, 1288 w cm^{-1} . (iii) Electronic absorption spectrum (CH_2Cl_2): ~ 700 w, 520 w, sh, 427 s nm. (iv) ¹H NMR (CD_3CN): δ 6.65 (doublet, $J_{\text{P-H}} = 497$ Hz), 2.38 (multiplet), 1.34 (multiplet), -3.71 (singlet).

(28) Katovic, V.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1268.

(29) Trogler, W. C.; Erwin, D. K.; Goeffroy, G. L.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 1160.

(30) Ebner, J. R.; McFadden, D. L.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 3014.

(31) A further piece of evidence in support of the formulation of $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$ concerns the similarity of the electrochemical properties of these two salts to those of the structurally characterized pyridinium salt $(\text{pyH})_3\text{Mo}_2\text{Cl}_8\text{H}$.²⁶ The cyclic voltammogram (CV) of $(\text{Et}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$ in 0.2 M tetra-*n*-butylammonium hexafluorophosphate-dichloromethane reveals an irreversible oxidation at $E_{\text{pa}} = +1.06$ V, a reversible couple at $E_{1/2} = +0.30$ V (corresponding to an oxidation), and an irreversible reduction at $E_{\text{pc}} = -1.00$ V (all potentials referenced to the SCE). The tri-*n*-propylphosphonium salt has a CV almost identical with this. While $(\text{pyH})_3\text{Mo}_2\text{Cl}_8\text{H}$ is insufficiently soluble in CH_2Cl_2 to record its CV in this solvent, solutions in 0.2 M TBAH-acetonitrile exhibit a reversible oxidation at $E_{1/2} = +0.35$ V, an irreversible oxidation at $E_{\text{pa}} = +1.05$ V and an irreversible reduction at -0.50 V, with only the latter process occurring at a potential much different from that which is observed in the CV's of $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$.

Table I. Relative Abundance of Major Ions in the SIMS Spectra of Phosphonium and Phosphine Complexes of Molybdenum and Rhenium^a

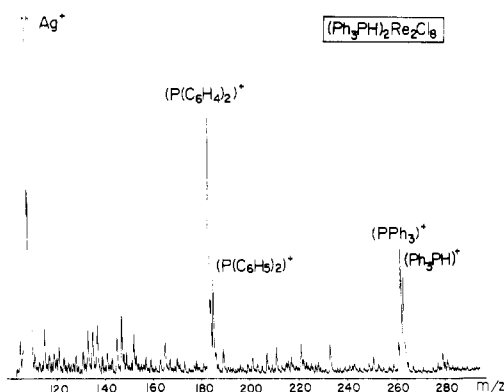
| complex | rel abundance ^b | | | | |
|---|--|------------------------------|------------------------------|----------------------|-----------------------|
| | [P(C ₆ H ₄) ₂] ⁺ | [L - H] ⁺ | [L] ⁺ | [L + H] ⁺ | [L + Ag] ⁺ |
| (Et ₃ PH) ₃ Mo ₂ Cl ₈ H | | 4 | 2 | 100 | 3 |
| (Et ₃ PH) ₂ Re ₂ Cl ₈ | | 6 | 7 | 100 | |
| (<i>n</i> -Pr ₃ PH) ₃ Mo ₂ Cl ₈ H | | 7 | 2 | 100 | <i>c</i> |
| (Ph ₃ PH) ₂ Re ₂ Cl ₈ | 100 | 12 | 46 | 38 | 17 |
| Mo ₂ Cl ₄ (PEt ₃) ₄ | | 48 | 14 | 100 | |
| [Mo(CNCMe ₃) ₆ (PEt ₃)](PF ₆) ₂ | | 58 | 25 | 100 | |
| Re ₂ Cl ₆ (PEt ₃) ₂ | | 49 | 31 | 100 | |
| Mo ₂ Cl ₄ (P- <i>n</i> -Pr ₃) ₄ | | 54 | 12 | 100 | |
| ReCl ₄ (P- <i>n</i> -Pr ₃) ₂ | | 66 | 7 | 100 | 15 |
| Mo ₂ Cl ₄ (PBU ₃) ₄ | | 52 | 12 | 100 | |
| ReCl ₃ (PMe ₂ Ph) ₃ | | 8 | 3 | 100 | |
| MoCl ₄ (PEtPh ₂) ₂ | 100 | 9 | 12 | 65 | <i>c</i> |
| Re ₂ Cl ₆ (PPh ₃) ₂ | 100 | 6 | 16 | 9 | |
| ReOCl ₃ (PPh ₃) ₂ | 100 | 6 | 35 | 23 | 3 |
| ReH ₅ (PPh ₃) ₃ | 100 | 15 | 58 | 29 | |
| Re ₂ H ₈ (PPh ₃) ₄ | 100 | 5 | 14 | 15 | 10 |
| ReH ₅ (PPh ₃) ₂ py | 100 | 9 | 27 | 19 | 14 |
| ReH ₅ (PPh ₃) ₂ (PEt ₂ Ph) | 100 | (<i>d</i> /17) ^e | (<i>d</i> /34) ^e | (25/17) ^e | (14/9) ^e |

^a All complexes were analyzed on silver foil with primary ion currents of 10⁻¹⁰ A/mm² or less. ^b L = phosphine. ^c Spectrum was not obtained to higher mass. ^d Abundance could not be accurately measured due to background interference. ^e Ratio of the abundance of ions derived from PEt₂Ph to that of the ions derived from PPh₃.

the trialkylphosphonium salts are (1) a doublet centered at $\delta \sim 6.65\text{--}6.88$ ($J_{\text{P-H}} \approx 498$ Hz) due to the unique proton of the R₃PH⁺ cations and (2) an upfield resonance at $\delta -3.71$ (R = Et) and $\delta -3.62$ (R = *n*-Pr) due to the bridging hydride ligand in the [Mo₂Cl₈H]³⁻ anions. This is the first time that the latter resonance has been identified for [Mo₂Cl₈H]³⁻, although the ¹H NMR signals of μ -H ligands in (Ph₃PH)[W₂Cl₆(μ -SMc₂)₂(μ -H)]³² and [W₂(μ -H)(O-*i*-Pr)₇]₂³³ have been reported, albeit at much lower fields.

(b) **Secondary Ion Mass Spectra (SIMS) of (R₃PH)₃Mo₂Cl₈H and Other Phosphonium Salts and Phosphine Complexes.** The SIMS spectrum of (Et₃PH)₃Mo₂Cl₈H exhibited an intense peak corresponding to [Et₃PH]⁺. In order to ensure that this ion was derived by the direct sputtering of a preformed cation and was not due to the protonation of neutral phosphine ligands during the SIMS experiment, we analyzed the dinuclear species Mo₂Cl₄(PEt₃)₄ for comparison. The SIMS spectra of both (Et₃PH)₃Mo₂Cl₈H and Mo₂Cl₄(PEt₃)₄ are presented in Figure 1. With the employment of nominally identical conditions of sample preparation, instrumental settings, and optimization procedure, the ion corresponding to [Et₃PH]⁺ is reproducibly observed in an approximate 10-fold excess in relative abundance for (Et₃PH)₃Mo₂Cl₈H compared to Mo₂Cl₄(PEt₃)₄. These results support the notion that the product of the reaction between Mo₂(mhp)₄, gaseous HCl, and triethylphosphine in alcoholic solvents is indeed (Et₃PH)₃Mo₂Cl₈H.

To ascertain the general applicability of this characterization technique, we analyzed a number of compounds of molybdenum and rhenium containing phosphonium ions or neutral phosphine ligands. The complexes analyzed and the relative abundances of major ions are given in Table I. The SIMS spectra of (R₃PH)₃Mo₂Cl₈H, where R = Et or *n*-Pr, and (Et₃PH)₂Re₂Cl₈ exhibit a single intense peak corresponding to [R₃PH]⁺. No metal-containing ions were observed in the positive-ion mode. (Et₃PH)₂Re₂Cl₈ and Re₂Cl₆(PEt₃)₂ also exhibit similar differences in the abundance of the [Et₃PH]⁺ ion as does the previously described molybdenum system (Et₃PH)₃Mo₂Cl₈H vs. Mo₂Cl₄(PEt₃)₄ (vide supra). A notable observation in these experiments is the appearance of the [L

Figure 2. SIMS spectrum of (Ph₃PH)₂Re₂Cl₈.

- H]⁺ ion in significant abundance (where L is an alkylphosphine) for complexes where the phosphine is present in its neutral form. The [L - H]⁺ ion is also seen in the SIMS spectra of alkylphosphonium salts but in much lower relative intensity compared to the corresponding [L + H]⁺ ion. This phenomenon is consistent for every sample analyzed and may constitute an empirically useful indication of the nature of the sample species. The [L + H]⁺/[L - H]⁺ ratio typically differs by one order of magnitude between trialkylphosphonium- and neutral trialkylphosphine-containing species (see Table I) and appears to be relatively insensitive to changes in the primary ion current from 1 × 10⁻¹¹ to 1 × 10⁻⁹ A/mm² and the energy of the argon beam (2.5–4.5 keV). These results imply that the [L - H]⁺ ion originates from the neutral ligand itself as opposed to hydrogen loss from the protonated species.

As with the electron impact (EI) mass spectra of alkyl- and arylphosphines,³⁴ the major ions of the SIMS spectra of complexes that contain arylphosphines are significantly different from those of their alkyl counterparts. This distinction results (at least in the case of the EI mass spectra) from the tendency of arylphosphines to undergo skeletal rearrangements upon impact to form stable 9-phosphafluorenyl ions such as P(C₆H₄)₂⁺ and P(C₆H₅)₂⁺.³⁵ In the SIMS spectrum of (Ph₃PH)₂Re₂Cl₈, the P(C₆H₄)₂⁺ and P(C₆H₅)₂⁺ ions are observed in 100 and 36 relative abundance, respectively. The [Ph₃PH]⁺ ion is also observed, but in this case the un-

(32) Boorman, P. M.; Moynihan, K. J.; Kerr, K. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1286.

(33) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. J. *Am. Chem. Soc.* **1981**, *103*, 779.

(34) *Chem. Anal. (N.Y.)* **1972**, *37*, Chapter 6.

(35) Granoth, I. *Top. Phosphorus Chem.* **1976**, *8*.

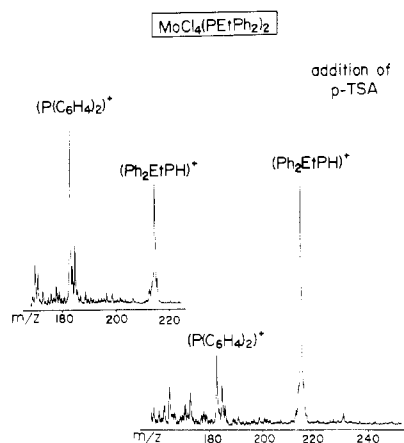


Figure 3. SIMS spectrum of $\text{MoCl}_4(\text{PEtPh}_2)_2$ illustrating the effect of acid on the intensity of the $[\text{R}_3\text{PH}]^+$ ion.

protonated $[\text{PPh}_3]^+$ is the more abundant of the two (Figure 2). The appearance of an ion corresponding to the unprotonated phosphine in greater abundance than its protonated form is unique to the triphenylphosphine derivatives studied. The observed ions are consistent with the electron impact (EI) results reported for triphenylphosphine, but the fragmentation is more extensive with the SIMS technique.^{36,37}

Compounds that contain preformed triphenylphosphonium ions such as $(\text{Ph}_3\text{PH})_2\text{Re}_2\text{Cl}_8$ and those that contain coordinated triphenylphosphine such as $\text{ReOCl}_3(\text{PPh}_3)_2$ give very similar SIMS spectra. One explanation for this is that $[\text{Ph}_3\text{PH}]^+$ as well as $[\text{PPh}_3]^+$ readily undergoes rearrangement to give the more stable $\text{P}(\text{C}_6\text{H}_4)_2^+$ and $\text{P}(\text{C}_6\text{H}_5)_2^+$ ions. Thus even though the cation $[\text{Ph}_3\text{PH}]^+$ would be expected to be sputtered with greater efficiency than the neutral triphenylphosphine ligand, the instability toward fragmentation reduces its intensity and does not allow for the differentiation between compounds containing $[\text{Ph}_3\text{PH}]^+$ and coordinated PPh_3 . This result contrasts with the differentiation between $[\text{R}_3\text{PH}]^+$ and $\text{M}-\text{PR}_3$ ($\text{R} = \text{alkyl group}$).

Several rhenium hydride complexes of triphenylphosphine, including $\text{Re}_2\text{H}_8(\text{PPh}_3)_4$ and $\text{ReH}_5(\text{PPh}_3)_3$, were analyzed (Table I). The results are typical of those observed for other triphenylphosphine complexes, and no species indicative of the presence of the hydrido ligands were observed. The SIMS spectrum of $\text{ReH}_5(\text{PPh}_3)_2(\text{PEt}_2\text{Ph})$ indicated the presence of both phosphine ligands in the form of the ions $[\text{PhEt}_2\text{PH}]^+$,

$[\text{PPh}_3]^+$, and $[\text{Ph}_3\text{PH}]^+$ as well as the silver cationized species $[\text{PEt}_2\text{Ph} + \text{Ag}]^+$ and $[\text{PPh}_3 + \text{Ag}]^+$. However, the $\text{PPh}_3/\text{PEt}_2\text{Ph}$ stoichiometric ratio in this complex was not discernible from the relative intensities of ions arising from the PPh_3 and PEt_2Ph ligands.

In an attempt to enhance the intensity of identifying ions in complexes containing neutral phosphine ligands, "derivatization" to yield a precharged entity was invoked. A drop of *p*-toluenesulfonic acid (*p*-TSA) dissolved in ethanol was added directly to the sample burnished on silver foil in an attempt to protonate the neutral phosphine ligand in order to observe it as $[\text{R}_3\text{PH}]^+$ in the SIMS spectrum. The addition of acid results in a significant enhancement of the $[\text{R}_3\text{PH}]^+$ signal as shown for $\text{MoCl}_4(\text{PEtPh}_2)_2$ in Figure 3. For this complex the signal enhancement also takes the form of an increase in intensity of $[\text{Ph}_2\text{EtPH}]^+$ over $[\text{P}(\text{C}_6\text{H}_4)_2]^+$, resulting in relative abundances of 100 and 28, respectively. Without acidification, relative abundances were 66 and 100, with $[\text{P}(\text{C}_6\text{H}_4)_2]^+$ as the more intense ion. The addition of *p*-TSA has virtually no effect on the $[\text{L} + \text{H}]^+ / [\text{L} - \text{H}]^+$ ratio in the case of trialkylphosphines.

(c) Conclusions. In the SIMS spectral studies that resulted from our characterization of the salts $(\text{R}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$, we have found that this technique can be useful in obtaining the exact mass of positively charged counterions whose characterization by conventional methods may not always be straightforward. SIMS can also be employed in the characterization of phosphine ligands for a variety of transition-metal complexes. The resulting spectra determine unambiguously which phosphine is present in a complex. Whether it exists as a phosphonium ion or a neutral ligand can be discerned through intensity comparisons.

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Registry No. $(\text{Et}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$, 83511-34-6; $\text{Mo}_2(\text{mhp})_4$, 67634-30-4; PEt_3 , 554-70-1; HCl , 7647-01-0; $(n\text{-Pr}_3\text{PH})_3\text{Mo}_2\text{Cl}_8\text{H}$, 83511-35-7; PPr_3 , 2234-97-1; $(\text{Et}_3\text{PH})_2\text{Re}_2\text{Cl}_8$, 83527-57-5; $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$, 14023-10-0; $(\text{Ph}_3\text{PH})_2\text{Re}_2\text{Cl}_8$, 83511-36-8; $\text{Re}_2\text{Cl}_6(\text{PPh}_3)_2$, 55722-73-1; PPh_3 , 603-35-0; $\text{ReCl}_4(\text{P-}n\text{-Pr}_3)_2$, 66808-71-7; $\text{Re}_2\text{Cl}_4(\text{P-}n\text{-Pr}_3)_2$, 55400-08-3; $\text{Mo}_2\text{Cl}_4(\text{PEt}_3)_4$, 59780-36-8; $[\text{Mo}(\text{CNCMe}_3)_3(\text{PEt}_3)](\text{PF}_6)_2$, 74096-91-0; $\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2$, 19584-31-7; $\text{Mo}_2\text{Cl}_4(\text{p-}n\text{-Pr}_3)_4$, 59780-37-9; $\text{Mo}_2\text{Cl}_4(\text{P}i\text{Bu}_3)_4$, 39306-31-5; $\text{ReCl}_3(\text{PMe}_2\text{Ph})_3$, 15613-32-8; $\text{MoCl}_4(\text{PEtPh}_2)_2$, 30411-58-6; $\text{ReOCl}_3(\text{PPh}_3)_2$, 17442-18-1; $\text{ReH}_5(\text{PPh}_3)_3$, 12104-75-5; $\text{Re}_2\text{H}_8(\text{PPh}_3)_4$, 66984-37-0; $\text{ReH}_5(\text{PPh}_3)_2\text{py}$, 25702-63-0; $\text{ReH}_5(\text{PPh}_3)_2(\text{PEt}_2\text{Ph})$, 25702-59-4.

(36) Miller, J. M. *J. Chem. Soc. A* **1967**, 828.

(37) Williams, D. H.; Ward, R. S.; Cooks, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 966.