to be diamagnetic. Both compounds are conductors of electricity with $\Lambda_{DMF} \doteq 41$ cm^2/(mol ohm). Such a value is consistent with a 1:1 electrolyte involving a gold complex.[14] In addition the electronic spectra of the complexes are nearly identical with that of $Au(mnt)_2^-$. The physical data allow the complexes to be formulated as mixed-valence systems consisting of equimolar portions of $Au(mnt)_2^-$ and $[(C_6H_5)_3Z]_2Au^+$, Z = P or As.

When preformed bis(triphenylphosphine)gold(I) chloride[15] was allowed to react with 1 molar equiv of tetra-*n*-butylammonium bis(maleonitriledithiolato)aurate(III), in tetrahydrofuran, a product of the composition $(C_6H_5)_3P$:Au:mnt = 1:1:1 was obtained. This complex was identical in all aspects with the one mentioned earlier in this paper. The same result was obtained in the case of the triphenylarsine complex when bis(triphenylarsine)gold(I) chloride was the gold(I) reactant.

The complex anion $Au(mnt)_2^-$ exhibits a maximum at 465 nm. A typical Beer–Lambert plot is obtained at this wavelength. The mixed-valence systems show a maximum wavelength very close to 465 nm. Since solutions containing $[(C_6H_5)_3Z]_2Au^+Cl^-$, Z = P or As, are colorless and transparent in the visible region of the electronic spectrum, it can be assumed that the transition observed near 465 nm for the mixed-valence systems is associated with $Au(mnt)_2^-$. By comparing absorption data obtained from solutions containing preweighed samples of the mixed-valence compounds to the Beer–Lambert plot for $Au(mnt)_2^-$ it is possible to determine the amount of $Au(mnt)_2^-$ present in the sample. In both cases the amount of $Au(mnt)_2^-$ present is less than the amount of sample present by an amount approximating $[(C_6H_5)_3Z]_2Au^+$, Z = P or As.[16]

The previous results are taken as further evidence for the formulation of the complexes as mixed-valence systems.

Recently we reported a reaction in which the authentic gold(II) complex $[(n\text{-}C_4H_9)_4N]_2Au(mnt)_2$ was isolated pure from reactants which consisted of equimolar portions of gold(I) and gold(III).[6] The gold-containing reactants were the mixed-valence compounds $[(C_6H_5CH_2)_2SAuX_3]$-$[(C_6H_5CH_2)_2SAuX]$, X = Cl or Br, and the solvent was degassed 90% THF–10% methanol. When the diamagnetic complexes $[(C_6H_5)_3Z]_2Au^+Au(mnt)_2^-$, Z = P or As, are allowed to react with excess Na_2mnt, in carefully degassed DMF, ESR spectra consisting of four lines are observed. The ESR g and $\langle a \rangle$ values are identical with those initially reported for $[(n\text{-}C_4H_9)_4N]_2Au(mnt)_2$.[5] Two possible mechanisms can be postulated for the formation of the Au^{II}–mnt anion. The first is a process in which $Au(mnt)_2^-$ is reduced to $Au(mnt)_2^{2-}$ by excess mnt^{2-} ligand. This path is ruled out, however, since ESR spectra are not observed when $(n\text{-}C_4H_9)_4NAu(mnt)_2$ and Na_2mnt are allowed to interact in degassed DMF. The second path involves a one-electron transfer between $Au(mnt)_2^-$ and a gold(I) complex containing the mnt ligand. Such a reaction can be formulated as in eq 1–3, where Z = P or As.

$$[(C_6H_5)_3Z]_2Au^+Au(mnt)_2^-(s) \rightarrow [(C_6H_5)_3Z]_2Au^+(soln) + Au(mnt)_2^-(soln) \qquad (1)$$

$$[(C_6H_5)_3Z]_2Au^+(soln) + 2mnt^{2-}(soln) \rightarrow 2(C_6H_5)_3Z(soln) + Au(mnt)_2^{3-}(soln) \qquad (2)$$

$$Au(mnt)_2^-(soln) + Au(mnt)_2^{3-}(soln) \rightleftharpoons 2Au(mnt)_2^{2-}(soln) \qquad (3)$$

In the present ESR experiments the molar ratio of $[(C_6H_5)_3P]_2Au^+$:excess mnt^{2-} was 0.502×10^{-1} and that of $[(C_6H_5)_3As]_2Au^+$:excess mnt^{2-} was 0.508×10^{-1}. In the former case the intensity of the ESR spectrum was assigned a value of 1.00 and the relative intensity of the latter was observed to be 1.28. The greater intensity of the ESR spectrum for the mixed-valence triphenylarsine complex can be attributed to (2) and (3). If the excess mnt^{2-} ligand in (2) displaces more triphenylarsine than triphenylphosphine from $[(C_6H_5)_3Z]_2Au^+$, more $Au(mnt)_2^{3-}$ will be generated for Z = As. Since the amount of $Au(mnt)_2^{2-}$ in (3) depends upon the amount of $Au(mnt)_2^{3-}$ produced in (2) a more intense ESR pattern would be expected for the Z = As system.

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Registry No. $(C_6H_5)_3PAuCl$, 14243-64-2; $(C_6H_5)_3AsAuCl$, 25749-29-5; $(C_6H_5)_3PAuCl_3$, 14243-66-4; $(C_6H_5)_3AsAuCl_3$, 17855-35-5; Na_2mnt, 18820-77-4; $[(C_6H_5)_3P]_2Au^+Au(mnt)_2^-$, 55925-82-1; $[(C_6H_5)_3As]_2Au^+Au(mnt)_2^-$, 55925-83-2; $(n\text{-}C_4H_9)_4NAu(mnt)_2$, 14710-21-5.

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Phosphorus(V) Chloride–Pyrazine Addition Compound

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It has been established that the compound of empirical formula PCl_5 exhibits three coordination numbers dependent upon the physical state and choice of solvent. Two competing equilibria have recently been reported[1] in ionizing solvents

$$2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$$

$$PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$$

In the solid state, a metastable crystal modification has been found and proposed[2] to incorporate chloride ions into the crystal lattice which would normally contain only PCl_4^+ ions and PCl_6^- ions.

Likewise, addition compounds formed with organic bases have been reported[3] wherein the variable coordination number about phosphorus is again encountered. For example, pyridine forms a molecular, 1:1 addition complex with PCl_5.[4,8] The addition of 2 equiv of pyridine to an acetonitrile solution of $PCl_4^+SbCl_6^-$ yields the postulated *cis*-$PCl_4(py)_2^+$ complex ion in solution.[5] Addition of 1,10-phenanthroline to $PCl_4^+SbCl_6^-$ forms the crystalline salt $PCl_4(phen)^+SbCl_6^-$. The phen molecule presumably acts as a cis bidentate ligand to the PCl_4^+ species filling the two remaining octahedral positions around phosphorus.[5,9] The variable coordination number of phos-

Table I. Molecular Weight Data

Molality	Depression of fp, °C	Apparent mol wt	Formula wt of $PCl_5(C_4H_4N_2)$
0.0299	0.181	147 ± 2	288
0.0630	0.376	148 ± 2	
0.0789	0.476	146 ± 2	

Table II. Conductivity Data

	Conductivity, ohm^{-1} cm^2 mol^{-1}	
Molarity	$PCl_4(C_4H_4N_2)^+Cl^-$	PCl_5
0.69	14.5	
0.89		10.4
0.0095	27.5	

phorus in these examples and the factors favoring the stability of each encourage further study.

With this in mind it was decided to investigate other nitrogen bases with respect to their coordination ability to phosphorus(V) chloride. Pyrazine, $C_4H_4N_2$, was chosen because of its known Lewis basicity toward both transition metal ions[6] and representative elements.[7] In addition, the presence of basic sites at both the 1 and 4 ring positions provides the possibility of trans polymeric species with PCl_4^+. Elemental analysis, molecular weight, electrical conductance, and proton NMR suggest, however, an ionic compound of 1:1 stoichiometry between PCl_5 and pyrazine.

Experimental Section

Pyrazine (pyr), obtained from Aldrich Chemical Co., was used without further purification. Phosphorus pentachloride (Matheson Coleman and Bell) was vacuum sublimed at 70° and handled exclusively in a drybox. Carbon disulfide (Baker) was stirred over P_4O_{10} for 48 hr and distilled at atmospheric pressure. The center fraction (bp 46°) was vapor transferred under vacuum to a glass storage bulb fitted with a Kontes high-vacuum Teflon stopcock. Nitromethane (Matheson Coleman and Bell) was purified by stirring over Davison 4-Å molecular sieves followed by distillation at 100.6° under nitrogen atmosphere and was stored in the drybox in a stoppered glass vessel. All solutions and samples were prepared either on a vacuum line or in a drybox to avoid contamination by atmospheric moisture.

Preparation of the PCl_5·pyr Adduct. To a solution of 2.0 g (10 mmol) of PCl_5 dissolved in 125 ml of CS_2 was added dropwise with stirring 0.8 g (10 mmol) of pyrazine dissolved in 15 ml of CS_2. A cloudy solution developed upon addition of all of the pyrazine. The white precipitate was stirred overnight, filtered under vacuum, and washed with freshly distilled CS_2 in a fritted vacuum extractor. An essentially quantitative yield was realized. Upon heating, the product darkened at 139° and then turned black at 160° and melted between 161 and 162°.

Analysis. Phosphorus and chlorine were determined gravimetrically after base hydrolysis of the sample as ammonium phosphomolybdate and silver chloride. Nitrogen was determined using a Kjeldahl method. Anal. Calcd for $PCl_5(C_4H_4N_2)$: P, 10.74; Cl, 61.48; N, 9.72. Found: P, 11.51; Cl, 60.87; N, 9.83. The nitrogen analysis was performed on a sublimed sample, whereas samples for phosphorus and chlorine analysis had not been sublimed.

Molecular Weight. Freezing point depression measurements were made on nitromethane solutions using an all-glass cell which allowed for constant stirring rate and complete isolation from the atmosphere. The temperature depressions were measured using a Sargent S-81615 thermistor in conjunction with a Sargent S-81601 thermometric bridge. Cooling curves were recorded on a Sargent recorder, Model SR. The system was calibrated using nitromethane solutions of naphthalene utilizing a cryoscopic constant, K_f, of 3.07° kg mol^{-1}. An ethylene dichloride slush (fp −35.6°) served as coolant.

Conductivity. Electrical conductance measurements of nitromethane solutions were carried out using a Leeds and Northrup No. 4960 portable electrolytic resistance indicator and a cell having a constant of 16.2 cm^{-1} at 25°.

Proton NMR. NMR samples were prepared and sealed under vacuum. Spectra were recorded on a Varian A60D NMR spectrometer equipped with a variable-temperature accessory. A single resonance was detected at τ 0.83 for the PCl_5·pyr complex in nitromethane. The appearance of the peak was unchanged down to −25°. However, upon successive addition of excess amounts of pyrazine at room temperature, the resonance shifted toward that of pure pyrazine at τ 1.38. A 1:1 solution of the complex and excess pyrazine in 1-nitropropane–nitromethane (5:1) yielded an unchanged NMR spectrum down to −100°.

Low-freezing solvents—butyronitrile, dimethylformamide, fluorotrichloromethane, and deuteriochloroform—were tried without success due to reaction with the solute or insolubility.

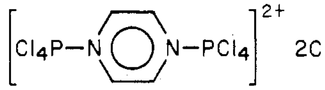
Results and Discussion

The compound formed by the reaction of pyrazine with phosphorus pentachloride is a white, crystalline, moisture-sensitive material. The analytical data support a 1:1 stoichiometry, but the cryoscopic molecular weight is within 2% of half the expected value of 288 based on the formula $PCl_5(C_4H_4N_2)$. This suggests either dissociation of the adduct in solution or the formation of ionic species. Complete dissociation in solution is ruled out by the fact that removal of solvent by pumping yields the adduct and not a mixture of PCl_5 and pyrazine. In addition, comparison of the proton NMR spectrum of the complex with that of pyrazine in the same solvent shows a downfield shift of 0.55 τ unit for the adduct protons. In the case of coordination to BF_3 reported by Fratiello, Schuster, and Geisel,[7] downfield shifts from uncoordinated pyrazine of 48 Hz for protons 3 and 5 and 12 Hz for protons 2 and 6 were observed. The average of these shifts is 30 Hz or 0.50 τ unit—approximately our observed shift. The single resonance of complexed pyrazine shifts upfield approaching that of uncomplexed pyrazine with the addition of excess amounts of pyrazine indicating an exchange process in solution. However, we see neither the 3, 5 vs. 2, 6 proton chemical shift differences nor the complexed vs. uncomplexed resonances at temperatures down to −100°. Furthermore, ionic species are suggested by conductance measurements in nitromethane. Comparison is made here to the equivalent conductance of phosphorus pentachloride which is known to have ions present in nitromethane solution.[1]

These data suggest a complex in which one pyrazine unit is bound to the PCl_4^+ ion with the anion being Cl^-. The mode of bonding between pyrazine and PCl_4^+, however, is not readily apparent. Several possibilities are considered.

Bonding through an electron pair on one nitrogen of the pyrazine ring to the phosphorus atom would give two sets of magnetically nonequivalent protons on the pyrazine ring as is seen in the complexes of BF_3 and BCl_3 with pyrazine.[7] The NMR spectrum of the PCl_5·pyr complex shows all protons of the pyrazine ring to be equivalent down to −100°. If a σ type N–P bond is present, the interaction is much weaker than that seen with BF_3 and pyrazine in which exchange is slowed sufficiently to show nonequivalence of ring protons at −10°.[7]

Bonding of one pyrazine molecule to each of two phosphorus units



would require a stoichiometry which is not supported by our analytical data.

Considering molecular dimensions, the transannular nitrogen distance in pyrazine,[10] 2.808 Å, compares favorably to the calculated Cl to Cl distance in the PCl_6^- octahedron, 2.93 Å, allowing the pyrazine ring to occupy two octahedral positions around phosphorus. However, the electron pairs on the two nitrogen atoms cannot both be directed toward one phosphorus atom. This eliminates the possiblity of simple dative bond formation by the lone pairs on the nitrogen atoms in an octahedral structure.

In considering the π system of pyrazine, the highest occupied molecular orbital of the ring has symmetry compatible with the empty $d_{x^2-y^2}$ orbital on phosphorus offering the possibility of bonding similar to that of the metal sandwich complexes. Such a π interaction is consistent with the single downfield ring proton resonance indicative of equivalent environments of the ring hydrogen atoms and may explain the facile nature of the exchange evidenced by our NMR results.

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Registry No. Pyrazine•PCl_5, 55975-46-7.

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Phosphorus-31 Nuclear Magnetic Resonance Spectra of *fac* and *mer* Isomers of Tricarbonylbis[bis(diphenylphosphino)methane]molybdenum

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The distinction between *fac* and *mer* isomers of $L_3Mo(CO)_3$ compounds is often made on the basis of infrared spectroscopy.[1-4] For certain ligands, notably phenyldimethylphosphine, proton NMR spectroscopy may distinguish the isomers, although not always conclusively.[4] In other phosphine ligands lacking such convenient alkyl groups (e.g., triphenylphosphine), proton NMR spectroscopy is of little stereochemical value. Such is the case with the ligand bis(diphenylphosphino)methane (dpm), for which we report here the *fac* and *mer* complexes $(OC)_3Mo(dpm)_2$. We show that ^{31}P NMR spectroscopy makes possible an unequivocal assignment of the isomers in this and presumably in other cases. Furthermore, the results are of interest in relation to recent studies of the ^{31}P spectra of chelating phosphines.

Experimental Section

Reagents. Bis(diphenylphosphino)methane purchased from Strem Chemicals Inc. was used without further purification. Preparation of $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_3$ followed a reported method.[5]

Physical Measurements. Infrared spectra of the carbonyl region were measured on a Perkin-Elmer Model 337 spectrometer equipped with an external recorder and were calibrated with bands of CO and DBr. The proton-decoupled ^{31}P NMR spectra were obtained on a Bruker HFX-90 operating at 36.4 MHz using a deuterium lock and a sealed capillary of P_4O_6 as an external standard. The chemical shift values are quoted relative to 85% H_3PO_4 which was taken to be 112.5 ppm upfield from P_4O_6. Microanalyses were performed by the Microanalytical Laboratory of this department.

Preparation of *fac*-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$. Bis(diphenylphosphino)methane (2.2 g, 5.7 mmol) and $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_3$ (0.5 g, 1.8 mmol) were dissolved in 50 ml of dichloromethane at room temperature. The solution turned pale yellow almost immediately and was stirred for 1 hr. After filtration, diethyl ether (50 ml) was added and the solution was chilled overnight at 0° to precipitate off-white crystals. These were recrystallized from dichloromethane–ether affording the analytical sample (yield 1.5 g, 86%, mp 178–180°). Anal. Calcd for $C_{55}H_{44}O_3P_4Mo$: C, 67.10; H, 4.67. Found: C, 66.88; H, 4.45. Infrared spectrum (ν_{CO} in cm^{-1}, relative intensities in parentheses): CH_2Cl_2, 1943 (10.0), 1848 (9.6, br); Nujol mull, 1938 (10.0), 1840 (10.0), 1825 (10.0).

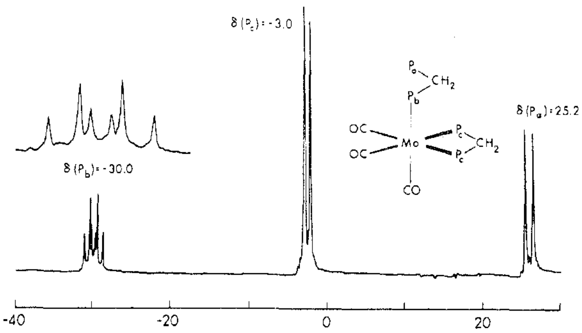

Figure 1. ^{31}P NMR spectrum of *fac*-$(OC)_3Mo(dpm)_2$ in CD_2Cl_2; chemical shifts in ppm relative to 85% H_3PO_4, with negative values downfield from reference. Coupling constants are $|^2J_{ab}| = 34.2$ Hz, $|^2J_{bc}| = 24.4$ Hz.

Preparation of *mer*-$(CO)_3Mo(Ph_2PCH_2PPh_2)_2$. Bis(diphenylphosphino)methane (2.2 g, 5.7 mmol) and $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_3$ (0.5 g, 5.7 mmol) were stirred in benzene (30 ml) for 15 min. Solvent was removed from the yellow solution under reduced pressure, and the residue was recrystallized from dichloromethane–ether affording yellow crystals of the *mer* isomer (yield 1.6 g, 91%, mp 184–186°). Anal. Calcd for $C_{55}H_{44}O_3P_4Mo$: C, 67.10; H, 4.67. Found: C, 66.70; H, 4.70. Infrared spectrum (ν_{CO} in cm^{-1}, relative intensitites in parentheses): CH_2Cl_2, 1969 (2.2), 1867 (10.0), 1841 (6.0, sh); Nujol mull, 1959 (6.0), 1858 (8.1, sh), 1845 (10.0).

Results and Discussion

The displacement of cycloheptatriene from $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_3$ by phosphines leads normally to the facial isomer of $(OC)_3MoL_3$.[6] Using dpm in dichloromethane at room temperature, we have obtained the anticipated *fac*-$(OC)_3Mo(dpm)_2$. However, the same reaction peformed at room temperature in benzene leads exclusively to the meridional form. Since isomerization of *fac* to *mer* is slow even in refluxing benzene, we conclude that the *fac* complex is not an intermeidate in the formation of the *mer* form in this solvent. This pronounced solvent effect is the more remarkable in view of the reported reaction of bis(diphenylstibino)methane with the cycloheptatriene complex in benzene to form *fac*-$(OC)_3Mo(Ph_2SbCH_2SbPh_2)_2$.[7]

The *fac* isomer is expected to show two carbonyl stretching bands (both strong) and the *mer* three (one strong) and the assignments made on this basis are in accord with those from ^{31}P NMR spectra (see below).

The ^{31}P NMR spectrum of *fac*-$(OC)_3Mo(dpm)_2$ is shown in Figure 1 and indicates three types of phosphorus atoms in the ratio 1:2:1. The doublet of triplets at lowest field is assigned to P_b, the coordinated phosphorus of the monodentate dpm; it is split into a doublet by the uncomplexed P_a which is further split into triplets by the two chemically equivalent atoms, P_c, of the chelate. The high-field doublet, which has a chemical shift very similar to that of free dpm, is assigned to the uncoordinated phosphorus atom P_a. The doublet at lower field corresponds to the chelating phosphorus atoms P_c.

The ^{31}P NMR spectrum of the *mer* isomer (Figure 2) shows four signals, since the phosphorus atoms of the chelate are no longer equivalent. The doublet at highest field is again assigned to the uncomplexed $P_{a'}$ while the doublet of quartets at lowest field must be assigned to P_b. The apparent triplet resonance is assigned to $P_{c'}$ which would be expected to have similar coupling constants to P_b and P_d since it is cis to both. The remaining resonance is a doublet of doublets as expected for P_d. The chemical shifts observed for the phosphorus atoms of chelated dpm are shielded by approximately 30 ppm as