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Rearrangements of Tetrahedral Copper(I) and Silver(I) Complexes Containing Chelating Bis(tertiary arsines and phosphines)

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Tetrahedral complexes of copper(I) and silver(I) of the type $[M(bidentate)_2]PF_6$ with (R^*,R^*)-(±)- or (R^*,S^*)-1,2-phenylenebis(methylphenylphosphine), and their arsenic isosteres, rearrange in solution by intermolecular ligand redistribution and by inversion of the tetrahedral metal stereocenters. The low barriers to inversion preclude optical resolution of the complexes into enantiomers chiral at the metal stereocenter, although ligand redistribution rates are slow enough under ambient conditions for the observation of diastereomers of the complexes in solution. Comparisons of the physicochemical properties of the copper(I) and silver(I) complexes of the bis(tertiary phosphine) with the previously studied gold(I) complexes revealed ligand redistribution rates increasing in the order gold(I) < copper(I) < silver(I). Equilibrium mixtures of diastereomers of complexes of the bis(tertiary arsine) are observed within the time of mixing of equimolar solutions of mirror-image enantiomers of complexes of all three metals. Metal stereocenter inversion barriers are low for all of the complexes studied with stabilities decreasing in the order copper(I) > gold(I) > silver(I)

Introduction

Relatively few experimental data are available concerning the stabilities of tetrahedral coordination compounds of tertiary phosphines and arsines. A study of gold(I) complexes of the type $[Au(bidentate)_2]PF_6$ with (R^*,R^*)-(±)- and (R^*,S^*)-1,2-phenylenebis(methylphenylphosphine) showed that the complexes were stable to ligand redistribution (intermolecular ligand exchange) in the absence of free ligand but that inversion barriers of the tetrahedral metal stereocenters in the complexes were low ($\Delta G^{\ddagger}_{393}$ = 78.2 kJ mol^{-1}).[1] Complexes of the corresponding bis(tertiary arsine) are more labile than those of the bis(tertiary phosphine) for gold(I), with ligand redistribution between diastereomers occurring within the time of mixing of mirror-image enantiomers of the same complex. Tetrahedral complexes of the type (±)-$[Au(bidentate)_2]X$, chiral at the metal stereocenter, with chelating bis(tertiary phosphines) and bis(tertiary arsines) are therefore unsuitable for optical resolution under normal conditions, thus corroborating the results of earlier work in this field.[2,3]

We have now examined the stabilities in solution of analogous complexes of copper(I) and silver(I) with the various forms of 1,2-phenylenebis(methylphenylphosphine) and their arsenic isosteres. Apart from the intrinsic interest in the nature of the tetrahedral metal stereocenter itself, complexes of this type are models for potential precursors of optically active quadridentate macrocycles and cages with resolved tertiary phosphine-*P* and tertiary arsine-*As* donor stereocenters. For example, stability studies on square-planar complexes of palladium(II) with related ligands preceded the synthesis of the first optically active chelating *trans*-As_2S_2 macrocycle.[4] A study of group IB metal ions with certain symmetrical and unsymmetrical tertiary phosphines has been published recently.[5]

Results and Discussion

Diasteromers and enantiomers of 1,2-phenylenebis(methylphenylphosphine) (diph)[6] and of the corresponding bis(tertiary arsine) (dias)[7] are depicted in Figure 1.[8] The complexes of the various forms of the ligands of the type $[Cu(bidentate)_2]PF_6$ were prepared from $[Cu(MeCN)_4]PF_6 \cdot 0.5H_2O$[9] by substitution reactions in acetonitrile. The corresponding silver(I) complexes were prepared from reactions of the various forms of the ligands with silver nitrate in 95% aqueous ethanol, followed by metatheses of the intermediate nitrate complexes with NH_4PF_6 (Table I).

Stereochemical Considerations. Diagrammatic representations of the diastereomers of $[M(bidentate)_2]^+$ are given in Figure 2. The optically active forms of the ligands produce discrete enantiomers of complexes of D_2 symmetry with equivalent P*Me* or As*Me* groups. The R^*,R^*-(±) forms of the ligands produce mixtures (provided the reactions are not completely stereoselective) of chiral (D_2) and achiral (S_4) complex cations. Interconversions between the diastereomers involve intermolecular rearrangments and thus are diagnostic of ligand redistribution. A convenient NMR test of metal-ligand bond strengths in complexes of the type $[M(bidentate)_2]^{n+}$ is therefore to mix together equimolar solutions of the mirror-image enantiomers of the same complex: the appearance of signals due to the achiral *meso complex* (in this case, one of S_4 symmetry) is definitive of bond breaking with intermolecular ligand exchange. Moreover, if the relative thermodynamic stabilities of the chiral and achiral diastereomers of a complex of a particular ligand are known with precision from studies with the racemic form of the ligand, the optical purity of a resolved form of the ligand can be determined by NMR spectroscopy.[3]

The achiral R^*,S^* diastereomers of the ligands produce discrete cations of C_2 symmetry with diastereotopic P*Me* or As*Me* groups. Thus, if it can be established with use of the R^*,R^*-(±) form of the ligand that a tetrahedral complex of a metal is stable with respect to *intermolecular* ligand redistribution under a given set of conditions, the failure to observe the diastereotopicity of the methyl groups in the ^1H NMR spectrum of the corresponding complex of the achiral R^*,S^* form of the ligand implies rapid *intramolecular* rearrangement of the tetrahedral metal stereocenter.

^1H NMR Studies. (a) Ligand Redistribution. The optically pure complexes of [*R*-(R^*,R^*)]-diph or [*R*-(R^*,R^*)]-dias with copper(I) and silver(I) display E*Me* singlets at 20 °C in dichloromethane-d_2 (Table I). The P*Me* resonances in the complexes of the bis(tertiary phosphine) are broadened due to unresolved coupling of the protons to the ^{31}P nuclei. When 0.06 M dichloromethane-d_2 solutions of mirror-image enantiomers of the

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Table I. Selected Physical Data and Elemental Analyses for Complexes

complex	mp, °C	Λ_M,[a] cm^2 Ω^{-1} mol^{-1}	$[\alpha]_D$,[b] deg	anal. % C[c]	anal. % H
$(-)\text{-}[\mathrm{Cu}([R\text{-}(R^*,R^*)]\text{-diph})_2]\mathrm{PF}_6{}^{d,e}$	213–215	92	−330 (0.396)	56.8 (56.5)	4.7 (4.9)
$(\pm)\text{-}[\mathrm{Cu}((R^*,R^*)\text{-diph})_2]\mathrm{PF}_6{}^{f}$	228–230	93		56.3 (56.3)	4.7 (4.7)
$(\pm)\text{-}[\mathrm{Cu}((R^*,S^*)\text{-diph})_2]\mathrm{PF}_6$	251–253	93		56.4 (56.3)	4.8 (4.7)
$(-)\text{-}[\mathrm{Cu}([R\text{-}(R^*,R^*)]\text{-dias})_2]\mathrm{PF}_6$	245–247	94	−200 (0.381)	46.9 (46.7)	4.0 (3.9)
$[\mathrm{Cu}((R^*,R^*)\text{-dias})_2]\mathrm{PF}_6{}^{d,g}$	207–209	92		47.1 (47.1)	4.1 (4.1)
$(\pm)\text{-}[\mathrm{Cu}((R^*,S^*)\text{-dias})_2]\mathrm{PF}_6{}^{h}$	258–260	92		46.1 (46.3)	4.0 (4.0)
$(-)\text{-}[\mathrm{Ag}([R\text{-}(R^*,R^*)]\text{-diph})_2]\mathrm{PF}_6$	234–236	93	−242 (0.336)	53.2 (53.5)	4.4 (4.5)
$[\mathrm{Ag}((R^*,R^*)\text{-diph})_2]\mathrm{PF}_6{}^{g}$	218–220	94		53.8 (53.5)	4.6 (4.5)
$(\pm)\text{-}[\mathrm{Ag}((R^*,S^*)\text{-diph})_2]\mathrm{PF}_6$	233–235	94		53.2 (53.5)	4.4 (4.5)
$(-)\text{-}[\mathrm{Ag}((R^*,R^*)\text{-dias})_2]\mathrm{PF}_6$	250–252	92	−137 (0.390)	44.8 (44.8)	3.8 (3.8)
$[\mathrm{Ag}((R^*,R^*)\text{-dias})_2]\mathrm{PF}_6{}^{g}$	213–215	93		44.7 (44.8)	3.7 (3.8)
$(\pm)\text{-}[\mathrm{Ag}((R^*,S^*)\text{-dias})_2]\mathrm{PF}_6$	211–213	92		44.2 (44.4)	3.8 (3.8)

[a] Conductivities measured at 293 K on 10^{-3} M solutions in acetonitrile. [b] Specific rotations measured at 293 K on acetone solutions at the concentrations specified in parentheses (g/100 mL). [c] Calculated values given in parentheses. [d] Complex isolated as the hemiacetone solvate. [e] Mirror-image enantiomers in each case have identical properties apart from equal and opposite specific rotations. [f] Complex isolated as the pure D_2 diastereomer (second-order asymmetric transformation); diastereomer rearranges above 213 K into an equilibrium mixture of D_2 and S_4 diastereomers. [g] Complexes of this type presumably crystallize as pure D_2 diastereomers, but all rearrange spontaneously into equilibrium mixtures of diastereomers upon dissolution at low temperatures. [h] Complex isolated as the hemihydrate.

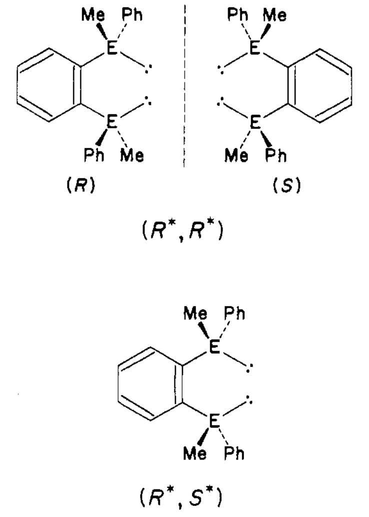

Figure 1. Diastereomers and enantiomers of 1,2-phenylenebis(methylphenylphosphine) (diph, E = P) and the arsenic analogue (dias, E = As).

Table II. Diagnostic ^{1}H NMR and Stability Data for the Complexes $[\mathrm{M}((R^*,R^*)\text{-bidentate})_2]\mathrm{PF}_6$ at 293 K

	δ(EMe)[a] D_2	δ(EMe)[a] S_4	D_2:S_4	$t_{1/2}$[b]
$(-)\text{-}[\mathrm{Cu}([R\text{-}(R^*,R^*)]\text{-diph})_2]\mathrm{PF}_6{}^{c}$	2.06			
$[\mathrm{Cu}((R^*,R^*)\text{-diph})_2]\mathrm{PF}_6$	2.06	1.37	1:6.0	20 min
$(-)\text{-}[\mathrm{Cu}([R\text{-}(R^*,R^*)]\text{-dias})_2]\mathrm{PF}_6$	1.94			
$[\mathrm{Cu}((R^*,R^*)\text{-dias})_2]\mathrm{PF}_6{}^{c}$	1.94	1.53	1:2.0	<1 min
$(-)\text{-}[\mathrm{Ag}([R\text{-}(R^*,R^*)]\text{-diph})_2]\mathrm{PF}_6{}^{c}$	1.97			
$[\mathrm{Ag}((R^*,R^*)\text{-diph})_2]\mathrm{PF}_6{}^{c}$	1.97	1.65	1:1.2	<1 min
$(-)\text{-}[\mathrm{Ag}([R\text{-}(R^*,R^*)]\text{-dias})_2]\mathrm{PF}_6{}^{c}$	1.87			
$[\mathrm{Ag}((R^*,R^*)\text{-dias})_2]\mathrm{PF}_6$	1.87	1.70	1:1.4	<1 min
$(-)\text{-}[\mathrm{Au}([R\text{-}(R^*,R^*)]\text{-diph})_2]\mathrm{PF}_6{}^{d}$	2.18			
$[\mathrm{Au}((R^*,R^*)\text{-diph})_2]\mathrm{PF}_6$	2.18	1.65	1:1.7	>1 month
$(-)\text{-}[\mathrm{Au}([R\text{-}(R^*,R^*)]\text{-dias})_2]\mathrm{PF}_6$	2.02			
$[\mathrm{Au}((R^*,R^*)\text{-dias})_2]\mathrm{PF}_6$	2.02	1.72	1:1.0	<1 min

[a] Chemical shifts relative to $\mathrm{Me_4Si}$ for 0.06 M $\mathrm{CD_2Cl_2}$ solutions of the complexes at 293 K. [b] Approximate half-lives for interconversions of D_2 and S_4 diastereomers of the complexes as determined by the mixing together of 0.06 M $\mathrm{CD_2Cl_2}$ solutions of the mirror-image enantiomers of the complexes at 293 K. [c] Complexes isolated as hemiacetone solvates. [d] Data for gold complexes taken from ref 1.

Table III. Diagnostic ^{1}H NMR and Stability Data for the Complexes $(\pm)\text{-}[\mathrm{M}((R^*,S^*)\text{-bidentate})_2]\mathrm{PF}_6$

	δ(EMe)[a]	T_c[b]	$\Delta G^{\ddagger}$[c]	$t_{1/2}$[d]
$(\pm)\text{-}[\mathrm{Cu}((R^*,S^*)\text{-diph})_2]\mathrm{PF}_6{}^{c}$	1.22, 2.15	>393	85.6[e]	230
$(\pm)\text{-}[\mathrm{Ag}((R^*,S^*)\text{-diph})_2]\mathrm{PF}_6$	1.54, 2.10	278	49.8	1×10^{-4}
$(\pm)\text{-}[\mathrm{Au}((R^*,S^*)\text{-diph})_2]\mathrm{PF}_6{}^{f}$	1.52, 2.26	393	78.2	11.6
$(\pm)\text{-}[\mathrm{Cu}((R^*,S^*)\text{-dias})_2]\mathrm{PF}_6{}^{g}$	1.44, 2.07	278	54.9	1×10^{-3}
$(\pm)\text{-}[\mathrm{Ag}((R^*,S^*)\text{-dias})_2]\mathrm{PF}_6{}^{g}$	1.68, 2.06	218	43.5	1×10^{-6}
$(\pm)\text{-}[\mathrm{Au}((R^*,S^*)\text{-dias})_2]\mathrm{PF}_6{}^{f}$	1.75, 2.13	244	48.9	1×10^{-4}

[a] Chemical shifts for diastereotopic E*Me* groups relative to $\mathrm{Me_4Si}$ for 0.06M dichloromethane-d_2 solutions of the complexes at 218 K. [b] Values of coalescence temperatures (T_c) in K; value of T_c above 300 K determined in nitrobenzene-d_5. [c] $\Delta G^{\ddagger}$ (kJ mol^{-1}) calculated from the Eyring equation by substitution of $k = \pi(\Delta\nu)/2^{1/2}$ and T_c.[11] [d] Values in seconds of $t_{1/2}$ for inversion at 25 °C calculated from k_{298} by substitution of $\Delta G^{\ddagger}$ values (determined at T_c) into the Eyring equation. [e] $\Delta G^{\ddagger}{}_{393}$ with k determined by line-shape analysis of variable-temperature spectra with use of DNMR3.[12] Use of $k = \pi(W - W_0)$ gives $\Delta G^{\ddagger}{}_{393}$ = 86.5 kJ mol^{-1}.[11] [f] Data taken from ref 1. [g] Complexes isolated as hemihydrates.

bis(tertiary phosphine)copper(I) complex are mixed together at 20 °C, the ^{1}H NMR signal for the P*Me* groups of the achiral S_4 diastereomer emerges with $t_{1/2}$ of ca. 20 min being required for the establishment of the D_2:S_4 = 1:6 equilibrium mixture of diastereomers. In acetonitrile-d_3 at 20 °C, D_2:S_4 = 1:1.3 at equilibrium; treatment of $[\mathrm{Cu(MeCN)_4}]\mathrm{PF_6}\cdot0.5\mathrm{H_2O}$ with 2 equiv of (R^*,R^*)-(±)-diph in acetonitrile-d_3 also gives the 1:1.3 equilibrium mixture of diastereomers. The dilution of an acetone solution of the copper(I) complex of (R^*,R^*)-(±)-diph (D_2:S_4 = 1:1.3 in acetone-d_6) with diethyl ether causes the crystallization of the pure D_2 complex in a typical second-order asymmetric transformation.[10] The pure D_2 complex can be dissolved in dichloromethane-d_2 at −60 °C without rearrangement; when the solution is warmed, however, the complex rearranges with $t_{1/2}$ of ca. 20 min at 20 °C being required for attainment of the D_2:S_4 = 1:6 equilibrium condition (for a 0.06 M solution). Complexes of silver(I) are more labile than the corresponding copper(I) complexes: the equilibrium D_2:S_4 = 1:1.2 mixture of diastereomers was established within the time of mixing (<1 min) of the mirror-image enantiomers of the bis(tertiary phosphine)silver(I) complex in dichloromethane-d_2 at 20 °C.

For the bis(tertiary arsine), equilibrium mixtures of the D_2 and S_4 diastereomers were formed within the time of mixing of equimolar solutions of the mirror-image enantiomers of the complexes of both metals. Proton NMR data for the complexes at equilibrium in dichloromethane-d_2 at 20 °C are summarized in Table I. Gold(I) complexes of the bis(tertiary arsine) underwent ligand redistribution with similar facility.[1]

(b) Metal Stereocenter Inversion. Ligand redistribution rates for all of the complexes studied are slow enough for the D_2 and S_4 complexes of the R^*,R^*-(±) forms of the ligands to be observed on the NMR time scale at 20 °C in dichloromethane-d_2. The

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[10] Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates, and Resolutions*; Wiley: New York, 1981; Chapter 6.

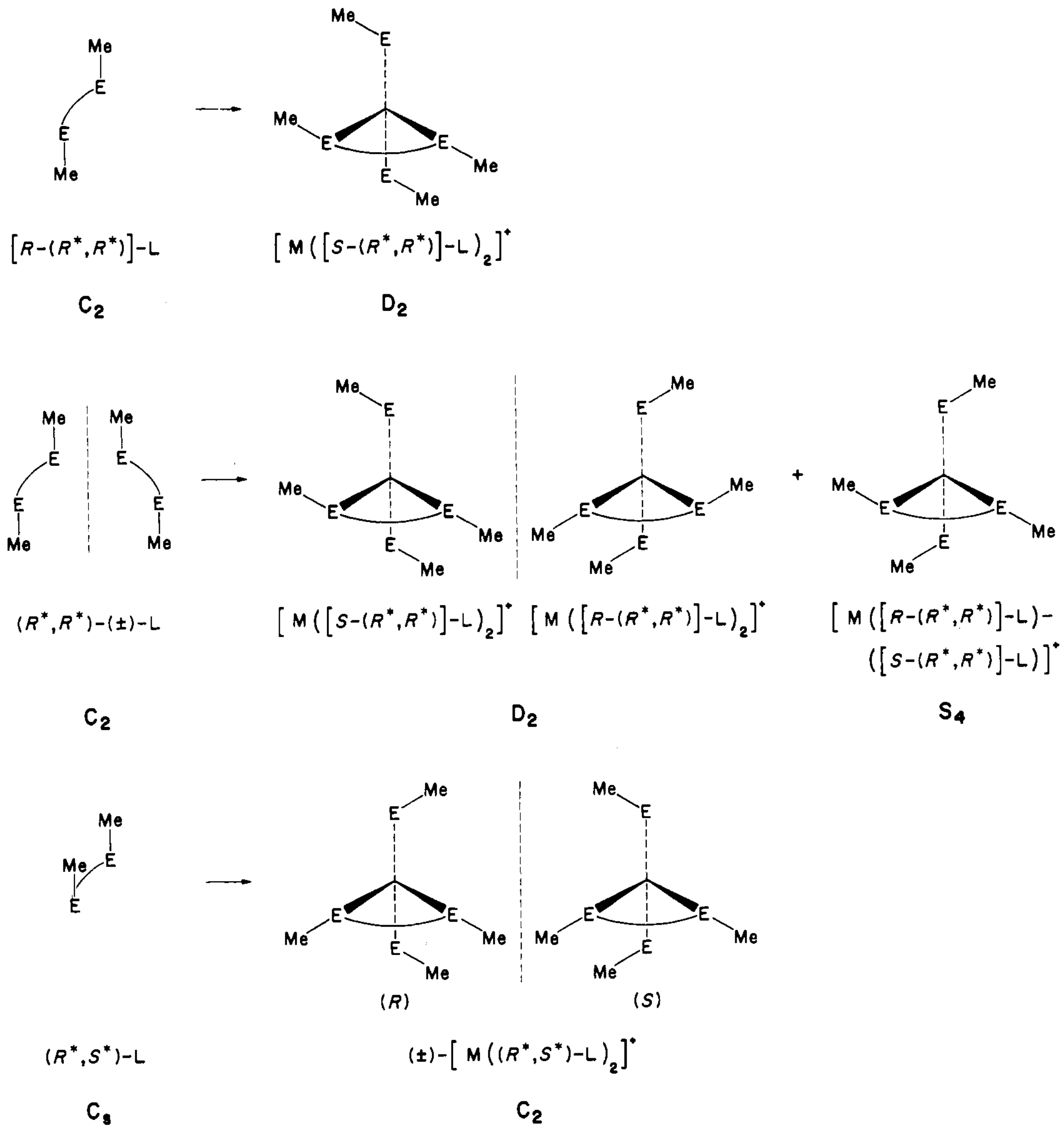

Figure 2. Stereochemical representations of tetrahedral cations of [M(bidentate)$_2$]PF$_6$.[14]

C_2 complexes of both metal ions with (R^*,S^*)-dias, and the silver(I) complex of (R^*,S^*)-diph, are, nevertheless, stereochemically nonrigid under these conditions, as demonstrated by the equivalence of the formally diastereotopic E*Me* groups in the ^{1}H NMR spectra of the complexes. The rigid structures can be "frozen-out" by lowering the temperature, however; coalescence temperature (T_c) for the rearrangements are given in Table II, along with ΔG^* values calculated by substitution of T_c and $k = \pi(\Delta\nu)/2^{1/2}$ into the Eyring equation.[11] Approximate half-life values for inversions of the metal stereocenters in the complexes at 25 °C are also given in Table II. The complex (±)-[Cu((R^*,S^*)-diph)$_2$]PF$_6$ is significantly more stable to internal rearrangement than the other three complexes, with heating to 120 °C of a nitrobenzene-d_5 solution of the complex being required for line broadening of the resonance of the diastereotopic P*Me* groups ($\Delta\nu_{1/2} = 3.5 \rightarrow 12$ Hz). The value of $\Delta G^*{}_{393}$ = 85.6 kJ mol^{-1} was calculated from the Eyring equation by substitution of rate constant k obtained from line-shape analysis of the variable-temperature ^{1}H NMR spectra with use of the computer program DNMR3.[12] Thus, metal stereocenter inversion is predominantly intramolecular in nature [$t_{1/2}$ = ca. 4 min (Table II); $t_{1/2}$(redistribution, 293 K) = 20 min] for [Cu(diph)$_2$]PF$_6$ (but not necessarily for [Ag(diph)$_2$]PF$_6$), although the present data do not permit meaningful comment on the mechanism of the rearrangement. Plausible processes for the intramolecular rearrangements include rupture of one or more of the metal–ligand bonds in the complexes or twisting of the metal chelate rings relative to one another via planar transition states.[13]

Conclusion

Four-coordinate bis(tertiary arsine) derivatives of univalent copper, silver, and gold are highly labile species in solution with intermolecular ligand redistribution between diastereomers of the same complex occurring within the time of mixing of mirror-image enantiomers of each complex. Ligand-exchange rates are slower for bis(tertiary phosphine) complexes, with rates decreasing in the order gold(I) > copper(I) > silver(I). Tetrahedral metal stereocenter inversion barriers are also low for complexes of all three metals ions for both tertiary arsines and tertiary phosphines with (±)-[Cu((R^*,S^*)-diph)$_2$]PF$_6$ having the highest barrier to inversion of any of the complexes studied ($\Delta G^\ddagger$ = ca. 86 kJ mol^{-1}; $t_{1/2}$ = 230 s at 25 °C). For each metal ion, the achiral tetrahedral meso complex of S_4 symmetry is more stable than the corresponding racemic complex of D_2 symmetry. Molecular models indicate less steric congestion in the S_4 structures, where E*Me*

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(11) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411–428.

(12) Binsch, G.; Kleier, D. A. *QCPE* **1969**, *10*, 140–146.

(13) Eaton, S. S.; Holm, R. H. *Inorg. Chem.* **1971**, *10*, 1446–1452.

(14) The replacement of a lone pair by a heavy metal changes the priority of that ligand (or phantom ligand) from 4 to 1; since this is an odd change (4 − 1 = 3), the CIP descriptor must be reversed when the ligand is coordinated to the metal and vice versa.[15]

(15) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–415.

groups alternate with E*Ph* groups around the peripheries of the complex ions. The D_2 structures have clashing pairwise arrangements of E*Me* and E*Ph* groups, consistent with the upfield chemical shifts observed for the E*Me* groups in the D_2 diastereomers. The equilibrium diastereoselectivities observed for the arsenic derivatives are lower than those observed for the phosphorus derivatives for copper(I) and gold(I), although silver(I) shows slightly higher discrimination with the arsenic ligand under the standard conditions employed. The greatest diastereoselectivity was found in the copper(I)–phosphorus system (D_2:S_4 = 1:6). Unfortunately, there are no solid-state structural data on the present series of complexes and data that are available on related complexes may not be applicable to these systems. Copper–donor atom bond lengths in $[Cu(Ph_2PCH_2CH_2PPh_2)_2]CF_3SO_3{\cdot}CH_3C_6H_5$ (2.31, 2.35 Å)[16] are shorter than those in $[Cu(1,2\text{-}C_6H_4(AsMe)_2)]PF_6$ (2.36 Å);[17] both structures have irregular interligand geometries. There are no structural data available for silver(I) complexes of bis(tertiary arsines) or bis(tertiary phosphines). The Au–P bond length in $[Au(Ph_2PCH_2CH_2PPh_2)_2]SbF_6{\cdot}Me_2CO$ is 2.40 Å;[18] in $[Au(1,2\text{-}C_6H_4(AsMe_2)_2)_2][Au(C_6F_5)_2]$ the Au–As bond length is 2.47 Å.[19] The well-known propensity of copper(I) for tetrahedral four-coordination and of gold(I) for linear two-coordination[20] may be the most important factor in the determination of diastereoselectivity and stability in these complexes. Thus, the greatest diastereoselectivities in solution would be expected for copper(I) systems, where discriminating steric effects would be maximized by four-coordination, particularly with chelating bis(tertiary phosphines).

Experimental Section

Proton NMR spectra of 0.06 M solutions were recorded on Bruker CXP-200 and Jeolco FX 200 spectrometers under the conditions stated. Optical rotations were measured on the specified solutions in 1-dm cells at 293 K with a Perkin-Elmer Model 241 polarimeter. Conductivity measurements were made at 293 K on 10^{-3} M solutions of the substances in acetonitrile with use of a Wissenschaftlich-Technische Werkstatten (D-8120 Weilheim, FRG) conductivity bridge. Elemental anlayses were performed by staff within the Research School of Chemistry.

The isolation of diastereomers and enantiomers of 1,2-phenylenebis(methylphenylphosphine)[6] and of the corresponding bis(tertiary arsine)[7] were carried out as previously described. Tetrakis(acetonitrile)copper(I) hexafluorophosphate hemihydrate was prepared by the method of Kubas.[9]

[*T*-4-[*R*-(*R,*R**)]]-Bis[1,2-phenylenebis(methylphenylphosphine)]-copper(I) Hexafluorophosphate Hemiacetone Solvate:** **(−)-[Cu([R-(*R**,*R**)]-diph)$_2$]PF$_6$·0.5Me$_2$CO.** A suspension of $[Cu(MeCN)_4]PF_6{\cdot}0.5H_2O$ (0.29 g) and [*S*-(*R**,*R**)]-diph (0.50 g)[14] in deoxygenated acetonitrile was stirred until a clear solution resulted. The colorless solution was filtered, and the filtrate was evaporated to dryness; recrystallization of the residue from an acetone–diethyl ether mixture gave the product as colorless needles, yield 0.55 g (83%).

[*T*-4-[*R*-(*R,*R**)]]-Bis[1,2-phenylenebis(methylphenylphopshine)]silver(I) Hexafluorophosphate, (−)-[Ag([*R*-(*R**,*R**)]-diph)$_2$]PF$_6$.** Silver(I) nitrate (0.13 g) was reacted with [*S*-(*R**,*R**)]-diph (0.50 g) in 95% ethanol (50 mL). The solution was evaporated to dryness, and the residue was redissolved in dichloromethane (50 mL). The dichloromethane solution was then treated with an aqueous NH_4PF_6 solution (1 g of NH_4PF_6, 20 mL of H_2O); the mixture was vigorously shaken, the layers were separated, and the organic layer was dried over $MgSO_4$. After filtration, the dried solution was taken to dryness and the colorless residue was recrystallized from an acetone–diethyl ether mixture. The product formed colorless needles, yield 0.58 g (82%).

The remaining compounds were obtained in high yields as colorless crystalline solids by following similar procedures. Details are given in the tables.

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Chemical Species in Sulfur–Ammonia Solutions: Influence of Amide Addition

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The acidity of sulfur–ammonia solutions has been modified by the introduction of an alkali-metal amide, and the chemical composition of the solution has been studied by using UV–visible spectrophotometry and Raman spectroscopy. It is shown that the progressive introduction of an alkali-metal amide makes the oxidized species more oxidized and the reduced species more reduced. It is found that, in sulfur–ammonia solutions, a chemical species less oxidized than S_4N^- exists in solution, which is neither S_7N^- nor a polysulfide; it is suggested that this species is a neutral form of sulfur. It is shown that the concentration of S_4N^- can be increased after amide addition by a factor of about 3 for a 10^{-2} M solution. Other oxidized forms of sulfur that have been observed are assigned to S_3N^- and S_2N^-. Very slow kinetics are observed for the modifications of the species induced by the introduction of the alkali-metal amide.

Introduction

Recent works related to sulfur–ammonia solutions have shown that the solutions contain the NH_4^+ cation and are therefore acidic.[1-5] It was shown that sulfur is solubilized in ammonia by a redox disproportionation mechanism, for which the following equations[1] have been proposed:

$$10S + 4\,NH_3 \rightarrow S_4N^- + S_6^{2-} + 3NH_4^+ \qquad (1)$$

$$S_6^{2-} \rightleftarrows 2S_3^- \qquad (2)$$

It was found later[2] that eq 1 does not describe completely the chemical species in sulfur–ammonia solutions; the existence of another oxidized species, S_3N^-, has been established by Raman spectroscopy. However eq 1 led us to investigate the influence of amide addition on the concentration of S_4N^- and of S_6^{2-}. It was found that the chemical species in solution can be modified and replaced by other species. In the present paper, the pH dependence of chemical species in solution is demonstrated, and the chemical species are tentatively identified. The increase of

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