Propeller Isomerism in Bis(trimesitylphosphine)gold(I), -silver(I), and -copper(I) Tetrafluoroborates

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Linear *two*-coordination of metals is a rare structural phenomenon restricted mainly to the heavy congeners in the copper and zinc triads.[1] While virtually all stereochemical aspects of the more common tetrahedral and octahedral coordination geometries were considered in extensive studies in the past,[2] very few attempts have been made to investigate steroisomerism at *two*-coordinate metal centers. The lack of information is largely due to a very limited number of suitable examples available for detailed investigation.

In the course of our studies of the coordination and organometallic chemistry of gold we recently prepared a series of 1:2 complexes of gold(I) with standard tri*alkyl*phosphines PR_3, which have the expected linear configuration at the metal center $[R_3P{-}Au{-}PR_3]^+$.[3,4] Owing to the high symmetry of these ligands with freely rotating alkyl groups (point group C_{3v}), no isomerism is expected in solution except for conventional conformational variations (staggered or eclipsed). The solid state structures reflect the 3-fold symmetry and indicate the preference for the staggered arrangement of the two PR_3 rotors in standard cases.[3−5]

The ground state structures of tri*aryl*phosphines have a reduced symmetry (point group C_3) and appear as chiral propellers which should induce isomerism even in complexes with a coordination number as low as 2. Such isomerism has not been observed in the past, because the phenyl groups or substituted phenyl groups in the triarylphosphine complexes which have been studied to date apparently rotate freely about the P−C bond axis in solution,[6] as judged from NMR experiments.

When the *aryl* groups are interlocked by *ortho*-substituents, however, the stereoisomerism becomes visible even in solution and already at ambient temperature. Four combinations of the two propellers have to be considered, one each with two left- or right-handed propellers, or with right/left or left/right directionality (R/R, L/L, R/L, and L/R). The first two cases have point group C_2 symmetry, while the latter two have point group C_i (staggered) or C_s (eclipsed) (Chart 1). The two phosphorus atoms (and their array of substituents) should be internally equivalent in all for cases, but the ligands in R/R and L/L should be inequivalent as compared to R/L and L/R. In high resolution NMR experiments the statistical (equilibrium) mixture of all stereoisomers in an isotropic medium should thus show two sets of ligand signals. Surprisingly, as far as we are aware, no attention has been paid to this aspect, and the presence of only one species was tacitly assumed in all pertinent cases.[5,6]

Bis(tri*mesityl*phosphine)gold(I) tetrafluoroborate, **1**, is readily prepared in quantitative yield from Mes_3PAuCl, Mes_3P, and $AgBF_4$ (molar ratio 1:1:1) in tetrahydrofuran/dichloromethane solution (colorless, air-stable solid, mp 232 °C). The $^{31}P\{^1H\}$ NMR spectra of solutions of this product in chloroform-d_1 at −60 °C show *two* sharp signals of equal intensity ($\delta = 5.2$ and 5.3 ppm), which collapse into *one* resonance as the solution is warmed to +30 °C ($\delta = 6.1$ ppm). This process is reversible upon cooling.

Owing to hindered rotation of the mesityl groups about the $P{-}C_{ipso}$ axes, the low temperature ^1H NMR spectra of the free Mes_3P ligand show three separate signals for the three 2,4,6-methyl groups and two signals for the 3,5-hydrogen atoms.[7] This is also observed for **1**, but in this case *two sets* of such ligand signals are obtained at −60 °C, which gradually merge into *one* set and are finally reduced further to three signals for the 2,6- and 4-methyl and 3,5-CH groups (relative intensity 6:3:2) upon heating. The chemical shift differences increase in the order $\delta(P) < \delta(CH) < \delta(CH_3)$; accordingly, the coalescence temperature is lowest for $\delta(P)$ and progressively higher for $\delta(CH)$ and $\delta(CH_3)$ signals. The spectral changes are readily explained by the proposed isomer distribution. From an analysis of the NMR data, the activation barrier for mesityl rotation in **1** is calculated to be $\Delta G^\ddagger = 63.6$ kJ mol^{-1} (15.2 kcal mol^{-1}). This value is higher than that for free Mes_3P (11.0 kcal mol^{-1}) and reflects the increased mesityl crowding in the complex, which is increased further in quaternary salts like $Mes_3PMe^+BF_4^-$ (17.4 kcal mol^{-1}), with smaller C−P−C angles at tetracoordinate phosphorus.[8]

To show that these findings can be generalized, the *silver(I)* and *copper(I)* homologues $[(Mes_3P)_2M]BF_4$ (M = Ag, **2**; M = Cu, **3**) were also prepared from $AgBF_4$ and 2 equiv of Mes_3P [colorless, air-stable crystals, mp 193 °C, **2**], and from CuCl, $AgBF_4$, and $2Mes_3P$ [mp 228 °C dec, **3**]. The $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$, −60 °C) of **2** show *four doublet resonances* due to $^{31}P{-}^{107/109}Ag$ coupling ($\delta = -28.9$ and -29.0 ppm, $J(P,Ag) = 508$ and 586 Hz in both cases). At +50 °C only two doublets remain after coalescence ($\delta = -27.5$ ppm, $J(P,Ag) = 517$ and 591 Hz). The ^1H NMR patterns are similar to those described for **1**. The fact that P,Ag coupling is retained in the temperature range from −60 to +50 °C is proof that the R/R−L/L vs R/L−L/R isomerization process is based on an *intra*molecular rearrangement with no metal−ligand dissociation. The individual propeller directionality is obviously

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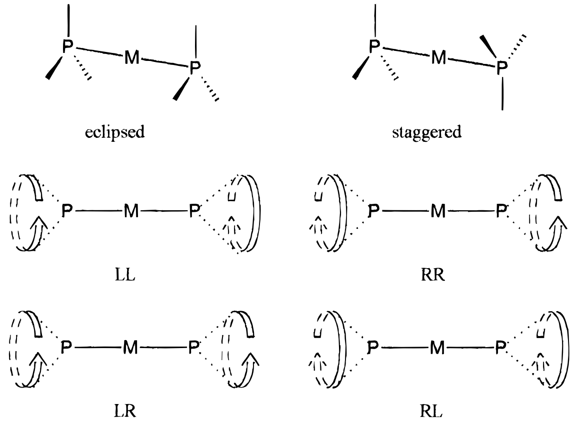
Chart 1



changed through concerted mesityl rotation, the mechanism of which has been delineated in elegant studies already in the 1970s and 1980s by Mislow et al.[9]

The copper compound **3** (in $CDCl_3$) has two ^{31}P resonances already at ambient temperature ($\delta = -29.7$ and -30.7 ppm, s) and two sets of ^{1}H signals similar to those of the gold homologue (**1**). With copper having the smallest covalent radius of the coinage metals, internal motions are most severely hindered in complex **3**, followed by **1** and **2**. Note that silver is the *largest* of the coinage metals![10]

Perhaps not unexpectedly, there appears to be a preference for one or the other individual isomer in crystal lattices, depending on the nature of the aryl group, the counterion, and the solvate molecules. Compounds **1** and **2** were obtained as single crystals (from CH_2Cl_2)[10] which both contained only cations with the R/R and L/L ligand configuration (staggered, point group C_2). By contrast, the less hindered cation $\{[(2\text{-Me-}C_6H_4)_3P]_2Au\}^+$ has the staggered C_i configuration (R/S, S/R) in the crystal of a bis(carborane)gold salt,[11] and the common $[(Ph_3P)_2Au]^+$ cation appears as a component of salts in all possible configurations and conformations.[12]

While the effects of restricted rotation of phosphine ligands about the metal−ligand bond, or of the substituents on the phosphine about the phosphorus−carbon bond have been observed previously by ^{31}P NMR spectroscopy in complexes containing a greater number of phosphine ligands,[13,14] the molecules concerned are usually too complex to allow a complete analysis of the spectra. The present results show that such an analysis is possible for the structurally simpler case of two-coordinate mononuclear complexes containing two equivalent phosphine ligands.

Experimental Part

General Data. All experiments were routinely carried out under an atmosphere of dry nitrogen. Solvents and glassware were dried and filled/saturated with nitrogen. NMR: Jeol GX 400 and GX 270 spectrometers; $CDCl_3$ solvent and phosphoric acid as internal and external standards, respectively; δ in ppm, J in Hz.

Bis[tris(2,4,6-trimethylphenyl)phosphine]copper(I), -silver(I) and -gold(I) Tetrafluoroborate (3, 2, 1). 3. A slurry of CuCl (20 mg, 0.20 mmol) in dichloromethane (20 mL) is treated with $(Mes)_3P$ (155 mg, 0.40 mmol) for 2 h at ambient temperature. A solution of $AgBF_4$ (39 mg, 0.20 mmol) in tetrahydrofuran (5 mL) is added to the resulting turbid solution (with protection against incandescent light) to precipitate AgCl. After filtration the mother liquor is concentrated in a vacuum and cooled to induce crystallization. Colorless crystals of a dichloromethane solvate are obtained (172 mg, 93% yield), mp 228 °C dec. Anal. Calcd for $C_{54}H_{66}BCuF_4P_2{\cdot}CH_2Cl_2$: C, 65.25; H, 6.77; Cu, 6.28. Found: C, 64.74; H, 6.75; Cu, 5.85.

2. $AgBF_4$ (39 mg, 0.20 mmol) is dissolved in tetrahydrofuran (5 mL), and $(Mes)_3P$ (155 mg, 0.40 mmol) is dissolved in dichloromethane (20 mL). The mixture of the two solutions is stirred for 6 h at ambient temperature with protection against incandescent light. The solvent is removed in a vacuum and the residue recrystallized from a mixture of CH_2Cl_2 and pentane [1:1] with cooling to give colorless, air-stable crystals (185 mg, 95% yield), mp 193 °C dec. Anal. Calcd for $C_{54}H_{66}AgBF_4P_2$: C, 66.75; H, 6.85; Ag, 11.10. Found: C, 67.80; H, 6.92; Ag, 10.50.

1. A solution of $AgBF_4$ (39 mg, 0.20 mmol) in thf (5 mL) and a solution of $(Mes)_3P$ (78 mg, 0.20 mmol) and $(Mes)_3PAuCl$ (124 mg, 0.20 mmol) in CH_2Cl_2 (20 mL) are mixed and stirred for 45 min at ambient temperature. The AgCl precipitate is filtered off, and the solvent is removed from the filtrate in a vacuum. The residue is taken up with a minimum volume of CH_2Cl_2 and the product precipitated by addition of pentane to give colorless crystals (207 mg, 98% yield), mp 232 °C dec. Anal. Calcd for $C_{54}H_{66}AuBF_4P_2$: C, 61.14; H, 6.27; Au, 18.57. Found: C, 59.95; H, 5.82; Au, 18.00.

$^{31}P\{^{1}H\}$ NMR spectra (A and B represent isomers RR/LL or RL/LR): **3** (25 °C), $\delta_A = -29.7$, δ_B -30.7 (s); **2** (−60 °C), $\delta_A = -28.9$, dd, $J_{Ag,P} = 508$ and 586 Hz, $\delta_B = -29.0$, dd, $J_{Ag,P} = 508$ and 586 Hz; **2** (+50 °C), $\delta = -27.5$, dd, $J_{Ag,P} = 517$ and 591 Hz; **1** (−60 °C), $\delta_A = 5.2$, $\delta_B = 5.3$ (s); **1** (+50 °C), $\delta = 6.3$ (s).

^{1}H NMR spectra (relative intensities are given, which refer to signals of the isomers RR/LL or RL/LR). **3** (+25 °C): $\delta = 6.88$ (3H) and 7.00 (1H), $HC_{3,5}$; $\delta = 1.80$ (6H), 2.09 (3H), and 2.12 (3H), $H_3CC_{2,6}$; $\delta = 2.31$ (3H) and 2.38 (3H), H_3CC_4. **2** (−60 °C): $\delta = 6.80$ (2H), 6.88 (1H), 6.97 (1H), $HC_{3,5}$; $\delta = 1.72$ (3H), 1.73 (3H), 2.05 (3H), and 2.10 (3H), $H_3CC_{2,6}$; $\delta = 2.24$ (3H) and 2.29 (3H), H_3CC_4. **2** (+50 °C): $\delta = 6.84{-}7.00$, br (2H), $HC_{3,5}$; $\delta = 1.78$ (3H) and 2.09 (3H), $H_3CC_{2,6}$; $\delta = 2.30$ (3H), H_3CC_4. **1** (−60 °C): $\delta = 6.82$ (2H), 6.90 (1H) and 7.01 (1H), $HC_{3,5}$; $\delta = 1.75$ (3H), 1.76 (3H), 2.25 (3H) and 2.27 (3H), $H_3CC_{2,6}$; $\delta = 2.28$ (3H) and 2.32 (3H), H_3CC_4. **1** (+50 °C): $\delta = 6.86{-}7.00$, br (2H), $HC_{3,5}$; $\delta = 1.83$ (3H) and 2.29 (3H), br, $H_3CC_{2,6}$; $\delta = 2.34$, br (3H), H_3CC_4.

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