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Steric Effects of Ligands in Silver(I) Isocyanide Complexes. Structure of $Ag(2,4,6\text{-}t\text{-}Bu_3C_6H_2NC)_2(PF_6)$ Containing a Bidentate PF_6 Ligand

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Reaction of $AgPF_6$ with RNC in a 1:2 molar ratio gave $Ag(RNC)_2(PF_6)$ 1 (R = $2,4,6\text{-}t\text{-}Bu_3C_6H_2$ (a), $2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}Me\text{-}C_6H_2$ (b), $2,6\text{-}Me_2C_6H_3$ (c), or t-Bu (d)). Reactions of (1b–d) with the corresponding isocyanide yielded $Ag(RNC)_3(PF_6)$ (2b–d), but the reaction of 1a with $2,4,6\text{-}t\text{-}Bu_3C_6H_2NC$ led to a recovery of the starting materials. The crystal structural analysis of 1a showed it to have a distorted tetrahedral configuration, in which a PF_6 ligand behaved as a bidentate ligand. The complex 1 exists as a 1:1 electrolyte in solution by a conductivity measurement [1].

Introduction

Steric effects of phosphorus ligands, described in terms of a ligand cone angle, have been documented by Tolman [2]. There are few examples for steric effects of isocyanide ligands. We have recently estimated the steric bulkiness of isocyanides in terms of a fan-shaped angle [3]. We reported that an increase of the fan-shaped angles of isocyanides led to a decrease of coordination number of ligand in the rhodium(I) isocyanide complexes.

We describe here the steric property of ligands in influencing the coordination number of the isocyanide ligands in silver isocyanide complexes. There are few studies on the isocyanide complexes of silver [4].

Results and Discussion

When $2,4,6\text{-}t\text{-}Bu_3C_6H_2NC$ was treated with $AgPF_6$ in a 2:1 molar ratio, the reaction gave white crystals formulated as $Ag(2,4,6\text{-}t\text{-}Bu_3C_6H_2NC)_2(PF_6)$ 1a. The infrared spectrum showed the three

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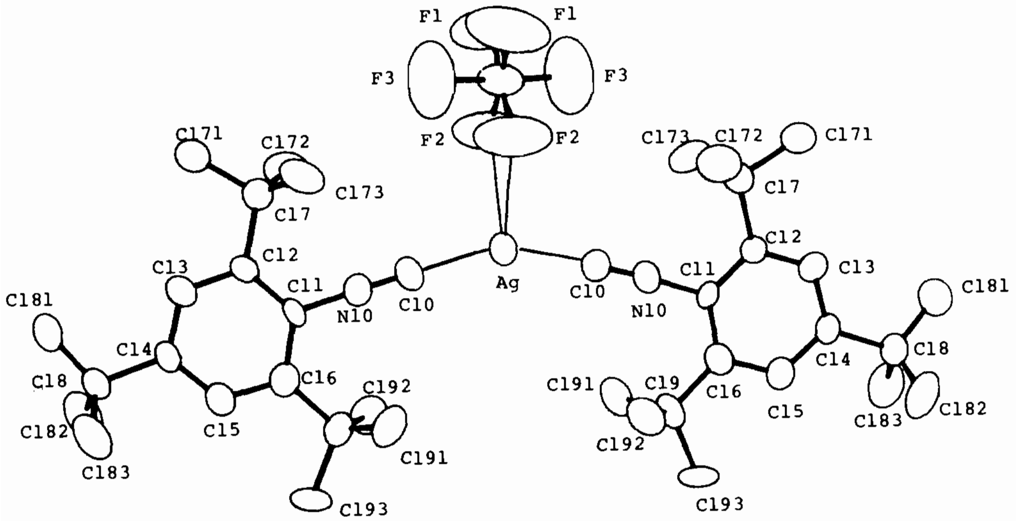

Fig. 1. Perspective view of non-hydrogen atoms showing the numbering scheme.

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N=C stretching bands at 2199, 2170, and 2122 cm^{-1} due to the terminal isocyanide groups. The ^{1}H nmr spectrum showed the presence of only one kind of isocyanide group. The similar type of complexes (1b–d) were also obtained from the reaction of 2,4-t-Bu_2-6-MeC_6H_2NC, 2,6-$Me_2C_6H_3NC$ or t-BuNC with $AgPF_6$ in a 2:1 molar ratio.

In an attempt to confirm an accurate structure, an X-ray crystallogrpahic analysis of 1a was carried out (*vide infra*). The complex has a distorted tetrahedral configuration coordinated to the silver atom by two isocyanide ligands and two fluorine atoms of the PF_6 group (Fig. 1). A similar type of coordination modes have been observed in $(CO)_5Re(FAsF_5)$ [5], . $(CO)_5Re(FBF_3)$ [6], and $IrHCl(CO)(PPh_3)_2(FBF_3)$ [7].

The conductivity of 1b in DMSO is 33 s cm^2 mol^{-1}, suggesting it to be a salt of 1:1 electrolyte type. Thus 1 exists as a neutral complex in the solid state and as a 1:1 electrolyte complex in solution.

The reactions of 1b–d with an excess of appropriate isocyanide gave the corresponding $Ag(RNC)_3(PF_6)$ (2b: R = 2,4-t-Bu_2-6-MeC_6H_2, 2c: R = 2,6-$Me_2C_6H_3$, 2d: R = t-Bu) (eqn. 1):

$$Ag(RNC)_2(PF_6) + RNC \rightarrow Ag(RNC)_3(PF_6) \qquad (1)$$

The conductivity of 2c in DMSO showed it again to be a 1:1 electrolyte complex; Λ_o = 34 s cm^2 mol^{-1}. We tentatively assigned that the complexes 2 were neutral in the solid state and a 1:1 electrolytes in solution on the basis of the structure of 1. Further reaction of 2 with isocyanide led to recovery of the starting materials.

The complex 1a did not react with 2,4,6-t-$Bu_3C_6H_2NC$, and was recovered.

This can be explained in terms of a steric effect of isocyanide. Increasing the size of ligand will lead to a severe repulsive interaction among ligands and then prevent expansion of the number of 2,4,6-tri-t-butylphenyl isocyanides having larger fan-shaped angles (width = 141° and thickness = 93°) [3] from ML_2X to ML_3X.

Crystal Structure of Ag(2,4,6-t-$Bu_3C_6H_2NC)_2(PF_6)$ 1a

Figure 1 is a perspective view of 1a. Bond distances and angles are given in Table I. The Ag–C10 bond length of 2.075(14) Å is within the sum of each covalent radii. The Ag–F2 distance of 2.668(14) Å is slightly longer than the sum (2.59 Å) of the covalent radii, but it can be regarded as a silver–fluorine interaction. This bond is slightly weak, this being explicable in terms of the fact that 1a dissociates readily to form a 1:1 electrolyte in solution. The angles, C10–Ag–C10 and F2–Ag–F2, were 156.1(1)° and 48.2(5)°, respectively. The dihedral angle between the C10AgC10 and F2AgF2 planes is *ca.* 87°. These results show that the molecular structure has an unusual tetrahedral configuration around the silver atom.

TABLE I. Selected Bond Distances and Angles.

Bond Distances (Å)			
Ag–C10	2.075(14)	C10–N10	1.148(17)
N10–C11	1.392(15)	Ag–F2	2.668(14)
P–F1	1.508(18)	P–F2	1.562(17)
P–F3	1.505(15)		
Bond Angles (°)			
C10–Ag–C10	156.1(6)	Ag–C10–N10	174.4(16)
C10–N10–C11	176.6(14)	F2–Ag–F2	48.2(5)
F1–P–F2	177.9(9)	F1–P–F3	85.5(12)
F2–P–F3	92.8(11)		

Experimental

Infrared spectra were recorded on a Shimazu IR-27G spectrophotometer. Proton magnetic spectra were obtained on JEOL C-60HL and Varian HA-100B spectrometers. Conductivity was measured by an Ando Electronic Company LCR-10 Type apparatus. Isocyanides were prepared by procedures described in the literature [3, 8].

Reaction of $AgPF_6$ with 2,4-t-Bu_2-6-MeC_6H_2NC

Ag(2,4-t-Bu_2-6-$MeC_6H_2NC)_2(PF_6)$ 1b. To a suspension of $AgPF_6$ (0.1 g, 0.4 mmol) in CH_2Cl_2 (10 ml) was added 2,4-di-t-butyl-6-methylphenyl isocyanide (0.19 g, 0.83 mmol) at room temperature. After 1 h, charcoal was added to the mixture and the solution was filtered through a glass filter. The solvent was removed *in vacuo*, and the residue was recrystallized from benzene–hexane to give white crystals of 1b (0.12 g, 81%, m.p. 205–207° (dec)). IR (KBr): 2159, 2111 (N≡C), 869 and 842 (P–F) cm^{-1}. NMR ($CDCl_3$): δ 1.32 (s, 4-t-Bu), 1.50 (s, 2-t-Bu), 2.49 (s, Me) and *ca.* 7.25 (c, aromatic protons) ppm. *Anal.* Found: C, 54.43; H, 6.61; N, 3.90. Calcd. for $C_{32}H_{46}N_2F_6PAg$: C, 54.02; H, 6.52; N, 3.94.

Other related compounds were also prepared according to procedures similar to those described above.

Ag(2,4,6-t-$Bu_3C_6H_2NC)_2(PF_6)$ 1a (73%, m.p. 234° (dec)). NMR ($CDCl_3$): δ 1.32 (s, t-Bu), 1.54 (s, o-Bu) and 7.37 (s, m-H) ppm. *Anal.* Found: C, 57.32; H, 7.37; N, 3.45; P, 3.87. Calcd. for $C_{38}H_{58}N_2F_6PAg$: C, 57.36; H, 7.35; N, 3.52; P, 3.89.

TABLE II. Crystallographic Data and Data Collection Parameters.

Formula	$C_{38}H_{56}N_2F_6PAg$
Space Group	C2/c
a, Å	20.022(8)
b, Å	10.829(7)
c, Å	20.023(6)
β, deg	106.4(1)
V	4164.9
Z	4
d_c/g cm^{-3}	1.176
(Mo Kα) cm^{-1}	3.11
Scan Type	$\omega-2\theta$
Collection Range	<45°
No. of Unique Data	1595
No. of Data I > 3σ(I)	1461
R_1[a]	0.089
R_2[a]	0.098

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $R_2 = [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$.

$Ag(2,6\text{-}Me_2C_6H_3NC)_2(PF_6)$ 1c (89%, m.p. 128–130 °C (dec)). IR (nujol): 2178 (N≡C) and 840 (P–F) cm^{-1}. NMR ($CDCl_3$): δ 2.49 (s, o-Me) and *ca.* 7.4 (c, aromatic protons) ppm. *Anal.* Found: C, 41.37; H, 3.36; N, 5.20. Calcd. for $C_{18}H_{18}N_2F_6PAg$: C, 28.66; H, 4.33; N, 6.68.

Reaction of 1b with 2,4-t-Bu-6-MeC$_6$H$_2$NC

2,4-Di-t-butyl-6-methylphenyl isocyanide (0.02 g, 0.086 mmol) was added to a solution of 1b (0.06 g, 0.08 mmol) in benzene (10 ml) at room temperature. After 1 h, the solvent was concentrated to *ca.* 3 ml and hexane was added to the solution. Colorless crystals of $Ag(2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_2NC)_3(PF_6)$ 2b (0.069 g (92%), m.p. 137–138° (dec)) were obtained. IR (KBr): 2158, 2109 (N≡C), 879 and 841 (P–F) cm^{-1}. NMR ($CDCl_3$): δ 1.32 (s, p-t-Bu), 1.51 (b, o-t-Bu), 2.47 (s, Me) and 7.17–7.4 (c, aromatic protons) ppm. *Anal.* Found: C, 61.39; H, 7.51; N, 4.47. Calcd for $C_{48}H_{69}N_3F_6PAg$: C, 61.27; H, 7.39; N, 4.47.

$Ag(2,6\text{-}Me_2C_6H_3NC)_3(PF_6)$ 2c (96%, m.p. 157–158° (dec)). IR (nujol): 2178 (N≡C) and 840 (P–F) cm^{-1}. NMR ($CDCl_3$): δ 2.50 (s, Me) and *ca.* 7.5

TABLE III. Final Atomic Parameters and Standard Deviations.[a]

Atom	X	Y	Z	B11	B22	B33	B12	B13	B23
Ag	0(0)	2177(2)	2500(0)	5(0)	8(0)	2(0)	0(0)	−1(0)	0(0)
P	0(0)	5460(7)	2500(0)	6(0)	7(1)	6(0)	0(0)	−2(0)	0(0)
F1	−505(8)	6438(13)	2589(11)	8(1)	14(2)	19(1)	3(1)	1(1)	−4(1)
F2	−501(8)	4426(12)	2613(10)	9(1)	11(1)	17(1)	2(1)	5(1)	0(1)
F3	−397(11)	5496(21)	1740(8)	14(1)	46(4)	6(1)	−2(2)	−4(1)	0(1)
N10	−826(7)	1508(11)	915(5)	4(0)	9(1)	2(0)	0(1)	1(0)	0(1)
C10	−562(9)	1779(14)	1483(8)	5(1)	8(2)	3(0)	1(1)	0(0)	0(1)
C11	−1166(7)	1118(13)	242(6)	3(1)	6(1)	1(0)	0(1)	0(0)	−1(1)
C12	−1382(7)	1988(12)	−280(6)	3(0)	6(2)	2(0)	−1(1)	1(0)	−1(1)
C13	−1703(8)	1606(14)	−954(7)	3(1)	8(2)	2(0)	0(1)	1(0)	−1(1)
C14	−1783(8)	360(13)	−1106(6)	3(1)	7(2)	2(0)	−1(1)	0(0)	−1(1)
C15	−1557(7)	−503(13)	−572(7)	2(1)	8(2)	2(0)	0(1)	1(0)	−1(1)
C16	−1228(8)	−173(14)	120(7)	3(1)	9(2)	2(0)	1(1)	1(0)	0(1)
C17	−1336(8)	3422(14)	−119(7)	3(1)	7(2)	3(0)	−2(1)	0(0)	0(1)
C18	−2120(10)	−106(15)	−1870(7)	7(1)	8(2)	2(0)	−2(1)	1(1)	−1(1)
C19	−991(8)	−1172(15)	681(7)	4(1)	9(2)	2(0)	0(1)	1(0)	1(1)
C171	−1734(8)	3793(16)	398(9)	3(1)	9(2)	5(1)	0(1)	2(1)	−2(1)
C172	−541(10)	3797(17)	138(10)	4(1)	10(2)	5(1)	−2(1)	2(1)	0(1)
C173	−1624(12)	4185(16)	−802(9)	9(1)	8(2)	3(1)	0(1)	0(1)	0(1)
C181	−2394(16)	928(19)	−2355(9)	15(2)	11(3)	2(1)	−2(2)	−2(1)	0(1)
C182	−1571(11)	−880(20)	−2098(9)	6(1)	19(3)	3(1)	−1(1)	3(1)	−3(1)
C183	−2744(10)	−983(19)	−1850(9)	5(1)	18(3)	4(1)	−5(1)	1(1)	−3(1)
C191	−176(8)	−1086(17)	979(8)	3(1)	12(2)	4(1)	1(1)	0(0)	2(1)
C192	−1363(10)	−1000(17)	1253(8)	5(1)	13(2)	3(1)	1(1)	2(1)	2(1)
C193	−1165(10)	−2503(12)	378(9)	5(1)	3(2)	5(1)	0(1)	1(1)	−1(1)

[a] Positional parameters are multiplied by 10^4. The form of the anisotropic thermal parameters is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{23}kl + 2B_{31}lh)]$ (10^3).

(aromatic protons) ppm. *Anal.* Found: C, 50.24; H, 4.23; N, 6.53. Calcd. for $C_{27}H_{27}N_3F_6PAg$: C, 50.17; H, 4.21; N, 6.50.

Ag(t-BuNC)$_3$(PF$_6$) 2d (95%, m.p. *ca.* 157° (dec)). IR (KBr): 2184 and 2241 cm^{-1}. NMR (CDCl$_3$): δ 1.59 (s, t-Bu) ppm. *Anal.* Found: C, 35.98; H, 5.49; N, 8.28. Calcd. for $C_{15}H_{27}N_3F_6PAg$: C, 35.87; H, 5.42; N, 8.37.

X-Ray Data Collection

The colorless crystals of Ag(2,4,6-t-Bu$_3$C$_6$H$_2$-NC)$_2$(PF$_6$) 1a were obtained from CH$_2$Cl$_2$–hexane. The X-ray intensity data were measured on a Rigaku-denki four-circle diffractometer with Mo-Kα radiation. The data were corrected for Lorentz and polarization effects, but not for absorption. Crystallographic data and data parameters are listed in Table II. Final atomic parameters and standard deviations are also listed in Table III.

The choice of space group C2/c was justified on the basis of the successful refinement of the structure. All atomic scattering factors were taken from the usual tabulations [9]. Anomalous dispersion effects for Ag, P and F were included in the calculation for Ic by using $\Delta f'$ and $\Delta f''$ calculated by Cromer.

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10 The following programs were used during the course of structure analysis. T. Sakurai and K. Kobayashi, Unics III: READ80, data reduction on a FACOM–200 computer; SC80, data scaling; File80; SFR£) and FPS80, structure factor calculation and Fourier synthesis; BDLS80, structure factor calculation and block-diagonal least-squares refinement; DA80, bond distances and angles; T. Ito: BP7A, least-squares planes.