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Preparation of Tris(phenylisocyanide)bis(triphenylarsine)cobalt(I) Perchlorate and Comparison with Tris(phenylisocyanide) bis (triphenylphosphine) cobalt (I) Perchlorate

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Introduction

Trialkylphosphites [1, 2], triarylphosphites [3], and triarylphosphines [1, 4] readily substitute in pentakis(arylisocyanide)cobalt(I) to produce mono- and/or disubstituted complexes depending on the phosphorus ligand, arylisocyanide, or reaction conditions; but triphenylarsine has not been observed to substitute in $[Co(CNR)_5]X$ (R = aryl; X = ClO_4, BF_4) [3]. $[Co(t\text{-}BuNC)_4AsPh_3]PF_6$ has been prepared by substitution reaction under prolonged refluxing in ethanol [5] however, and $[Co(CO)_3(AsPh_3)_2][Co(CO)_4]$ as well as $[Co(CO)_3AsPh_3]_2$ have been prepared [6]. $[Co(CNR)_4PPh_3]X$ and $[Co(CNR)_3(PPh_3)_2]X$ have also been prepared by reaction of RNC with $Co(PPh_3)_2X_2$ [7, 8], and $[Co(CNR)_3L_2]Y$ (L = $PhP(OEt)_2$, $P(OMe)_3$; Y = ClO_4, BF_4) prepared by reaction of RNC with $[CoXL_4]Y$ (X = Cl, Br, I) or simply a $CoCl_2$–phosphite mixture [9]. In view of this chemistry a one-stage reduction/ligand substitution reaction of excess $AsPh_3$ on $[Co(CNR)_5](ClO_4)_2\cdot xH_2O$ seems reasonable.

Experimental

Dichloromethane and chloroform were distilled over $Mg(ClO_4)_2$; anhydrous diethyl ether was filtered through an alumina column immediately before use. Commercial $AsPh_3$, PPh_3, $P(OMe)_3$ and $P(OPh)_3$ were used without purification. The $[Co(CNPh)_5](ClO_4)_2\cdot H_2O$ and $[Co(CNR)_5]X$ (X = ClO_4, BF_4) were prepared as previously described [10, 11]. Proton-NMR spectra were recorded on a Varian XL100 in $DCCl_3$ using CH_2Cl_2 as secondary internal reference (δ 5.28). Infrared spectra were recorded on a Beckman IR-33 in nujol mull and CH_2Cl_2 solution. Electronic spectra were recorded on a Unicam SP 1800 in CH_2Cl_2 solution (25 °C). Elemental analyses were performed by Ilse Beetz Microanalytical Laboratory.

Preparation of $[Co(CNPh)_3(PPh_3)_2]ClO_4$

A 0.290 g (0.364 mmol) sample of $[Co(CNPh)_5]ClO_4\cdot CHCl_3$ was dissolved in 1.0 ml CH_2Cl_2 and filtered through cotton. Then 0.480 g (1.82 mmol) PPh_3 in 1.0 ml CH_2Cl_2 was added rapidly dropwise. Odor of PhNC was evident almost immediately. After ten minutes reaction time, 2.0 ml ether was added dropwise to effect precipitation. The bright orange crystals were cooled in ice, filtered, and re-crystallized from 3.0 ml CH_2Cl_2 and 2.0 ml ether. Yield: 0.250 g (60%); m.p. 182–186 °C (decomposition). The $-N{\equiv}C$ IR: 2005w, 2065s(br), 2130w(sh) (Nujol); 2005w, 2070s, 2120vw(sh) cm^{-1} (CH_2Cl_2). This complex is atmosphere-stable and was desiccated several weeks before analysis. *Anal.* Calcd. for $CoC_{58.9}H_{48.8}Cl_{4.8}N_3O_4P_2$ (*i.e.*, $[Co(CNPh)_3(PPh_3)_2]ClO_4\cdot 1.9CH_2Cl_2$): C, 61.32; H, 4.26; N, 3.64; Cl, 14.75. Found: C, 62.04; H, 4.22; N, 3.50; Cl, 14.81. Proton-NMR integration, CNPh:PPh_3:CH_2Cl_2 = 3.00:1.91:2.10.

Reaction of $[Co(CNPh)_5]BF_4$ and $[Co(CNC_6H_4\text{-}Cl\text{-}p)_5]BF_4$ with five molar ratio of $AsPh_3$ was attempted in CH_2Cl_2 for short-term (*i.e.*, 15–20 min) and prolonged (*i.e.*, 3–4 hr) periods and in refluxing $CHCl_3$ (3 hr). For reactions at 25 °C the starting material was recovered in good yield (~ 90%) while at 62 °C there was some $[Co(CNPh)_5]BF_4$ decomposition, but no evidence of $AsPh_3$ substitution.

Preparation of $[Co(CNPh)_3(AsPh_3)_2]ClO_4$

A 1.50 g (1.90 mmol) sample of $[Co(CNPh)_5](ClO_4)_2\cdot H_2O$ was dissolved in 6.5 ml CH_2Cl_2, filtered through cotton, and chilled in ice. Then 2.91 g (9.50 mmol) $AsPh_3$ in 1.0 ml CH_2Cl_2 was added dropwise. The dark green solution turned red-brown almost immediately in this exothermic reaction. When addition was completed the solution was allowed to warm to 25 °C for ten minutes and filtered. Then 10.0 ml ether was added dropwise and the solution chilled in ice one day to produce ruby-colored crystals. Adding 4.0 ml ether to the filtrate and additional cooling afforded a second crop. Crude product was re-crystallized from $CHCl_3$/ether. Yield: 1.160 g (56%); m.p. 152–158 °C (decomposition). The $-N{\equiv}C$ IR: 2005w(sh), 2060s(br), 2120vw(sh) (Nujol); 2000 vw, 2065s, 2110vw(sh) cm^{-1} (CH_2Cl_2). This sample was dried one week *in vacuo* before analysis. *Anal.* Calcd. for $CoC_{57.15}H_{45.15}As_2Cl_{1.45}N_3O_4$ (*i.e.*, $[Co(CNPh)_3(AsPh_3)_2]ClO_4\cdot 0.15CHCl_3$): C, 62.51; H, 4.14; N, 3.83; Cl, 4.68. Found: C, 61.98; H, 4.18; N, 3.94; Cl, 4.56. Proton-NMR integration, CNPh:$AsPh_3$ = 3.00:2.13. Analogous preparation of $[Co(CNPh)_3(PPh_3)_2]ClO_4\cdot 2.0CH_2Cl_2$. Yield: 1.805 g (82%).

The $[Co(CNPh)_3(AsPh_3)_2]ClO_4\cdot xCHCl_3$ is ruby-red as well-formed crystals, which become chalky red-orange upon loss of adducted solvent. Freshly

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crystallized samples are probably $CHCl_3$-monosolvated or CH_2Cl_2-disolvated (from NMR and solubility data), but adducted solvent can be removed under sufficiently prolonged desiccation. The material is soluble in CH_2Cl_2 and $CHCl_3$, sparingly soluble in acetone and methanol and insoluble in water, ether and toluene. The complex is moderately atmosphere-stable, but decomposed over several months (presumably through Co(I) oxidation and CNPh polymerization).

Reactions of [Co(CNPh)$_3$(AsPh$_3$)$_2$]ClO$_4$ with Phosphorus Ligands

Three 0.110 g (~ 0.100 mmol) samples of $[Co(CNPh)_3(AsPh_3)_2]ClO_4 \cdot 0.15CHCl_3$ were dissolved in 1.0 ml CH_2Cl_2 and treated dropwise with 5:1 molar ratio of phosphorus ligand (*i.e.*, 0.131 g PPh_3/0.5 ml CH_2Cl_2, 0.062 g $P(OMe)_3$/equal volume CH_2Cl_2, and 0.155 g $P(OPh)_3$/equal volume CH_2Cl_2, respectively). After 15.0 min reaction time, during which the red solution exhbited appropriate color change (*i.e.*, orange, pale yellow, and dark yellow, respectively), the solution was filtered through cotton, and ether was added dropwise to effect precipitation (2.5, 3.0, and 4.0 ml, respectively). The crystals were cooled in ice, collected, and re-crystallized from CH_2Cl_2/ether; the compounds were readily identified from previous physical measurements [2, 3]. Yield: 0.091 g $[Co(CNPh)_3(PPh_3)_2]ClO_4 \cdot 2.0CH_2Cl_2$ (78%), 0.042 g $[Co(CNPh)_3\{P(OMe)_3\}_2]ClO_4$ (59%), and 0.080 g $[Co(CNPh)_3\{P(OPh)_3\}_2]ClO_4$ (79%), respectively.

Results and Discussion

While $[Co(CNPh)_3(AsPh_3)_2]ClO_4$ is not an unexpected compound, it is significant that $AsPh_3$ can replace PhNC in a short-term reduction/ligand substitution of $[Co(CNPh)_5](ClO_4)_2 \cdot H_2O$ while $AsPh_3$ fails to substitute in $[Co(CNR)_5]^+$ under more drastic conditions and only monosubstitutes in the more reactive $[Co(t\text{-}BuNC)_5]^+$ under reaction conditions too severe for arylisocyanides [5]. Reactions with $AsPh_3$ are thus unlike those with PPh_3. Disubstituted complex was either minor product (*i.e.*, 8.7% $[Co(CNC_6H_4Me\text{-}p)_3(PPh_3)_2]Cl$ *vs.* 53.5% $[Co(CNC_6H_4Me\text{-}p)_4PPh_3]Cl$) or produced in low yield (*i.e.*, 18.8% $[Co(CNC_6H_4Me\text{-}p)_3(PPh_3)_2]Br$ and 18.3% $[Co(CNC_6H_4Me\text{-}p)_3(PPh_3)_2]I$) in reaction of excess p-MeC_6H_4NC with $CoX_2(PPh_3)_2$ [8], so that reaction is not the same as the reduction/ligand substitution used here. This compound was also prepared under room conditions while $[Co(CO)_3(AsPh_3)_2][Co(CO)_4]$ required N_2(g)-atmosphere and disproportionated to $[Co(CO)_3AsPh_3]_2$ above 0 °C [6].

The (fundamental) $-N{\equiv}C$ stretch in $[Co(CNPh)_3(AsPh_3)_2]^+$ (2065 cm^{-1}) is at slightly lower frequency than in $[Co(CNPh)_3(PPh_3)_2]^+$ (2070 cm^{-1}) and at significantly lower frequency than in $[Co(CNPh)_5]^+$ (2114, 2151.5 cm^{-1}) [12] and PhNC (2133 cm^{-1}) [11b]. This indicates $AsPh_3$ is a slightly stronger σ-donating and/or weaker π^*-accepting ligand than PPh_3 and significantly more so than CNPh. In $[Co(CNPh)_3(AsPh_3)_2]^+$ the CNPh is accepting more electron density (through $d_\pi(M) \rightarrow \pi^*(L)$ bonding) than donating (through $\sigma(L) \rightarrow \sigma^*(M)$ bonding). An unfamiliar CNC_6H_5 pattern is observed in the ^1H NMR of $[Co(CNPh)_3(PPh_3)_2]^+$ since the signal for the *para*-proton, at δ 7.13, coincides with one component of the (approximate) AB pattern for *ortho*- and *meta*-protons (δ 5.85, 5.93, 7.05, 7.13; *i.e.* δ_1 5.89, δ_2 7.09), so the signal for CNC_6H_5 superficially resembles that observed for *para*-substituted phenylisocyanides [2, 11b]. The PPh_3 signal is split ($J \simeq$ 1.5 Hz) and centered at δ 7.54. The spectrum for $[Co(CNPh)_3(AsPh_3)_2]^+$, broadened due to probable trace-amounts of paramagentic decomposition-impurity, is interpreted by analogy. The CNC_6H_5 protons are observed δ 5.98-*o*, δ 7.19-*m*, δ 7.47-*p*. The $AsPh_3$ signal is a broad singlet at δ 7.68, downfield from the uncoordinated ligand (*i.e.*, δ 7.39/ $CDCl_3/CH_2Cl_2$). Only the signal attributed to the *ortho*-C_6H_5NC protons could be separately integrated, however, so this assignment is not unambiguous.

The electronic spectrum (450–230 nm, CH_2Cl_2, 25 °C) for $[Co(CNPh)_3(AsPh_3)_2]ClO_4$, maxima 334 m$\mu$ ($\epsilon \simeq$ 18,800), 248 mμ (57,400), 233 mμ (56,300) is compared to that for $[Co(CNPh)_3(PPh_3)_2]ClO_4$, 353 m$\mu$ (38,400), 285 mμ (44,600), 237 mμ (72,200) in Fig. 1. All bands are without Gaussian resolution and the third band is possibly distorted by proximity to the optical limit. The familiar three-band charge-transfer spectrum for five-coordinate Co(I) [2] is observed. Lower frequency for the first transition suggests that $[Co(CNPh)_3(PPh_3)_2]^+$ is more exten-

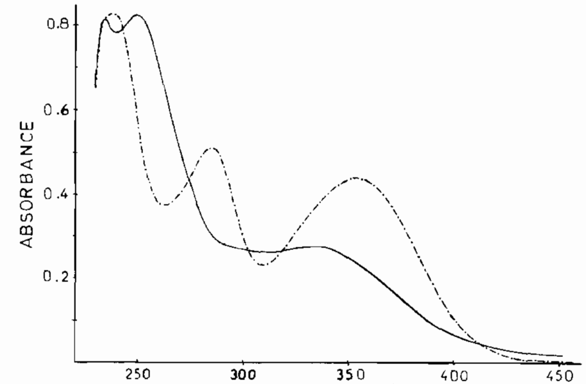

Fig. 1. Electronic spectra (CH_2Cl_2, 25 °C) for 1.44×10^{-5} *M* $[Co(CNPh)_3(AsPh_3)_2]ClO_4$ (——) and 1.14×10^{-5} *M* $[Co(CNPh)_3(PPh_3)_2]ClO_4$ (– · – · –).

sively π-bonded (without attempting to assign the transition), but a red-shift occurs for $[Co(CNPh)_3(AsPh_3)_2]^+$ because the lowest energy absorption tails much stronger into the visible region (note relative absorptions *circa* 450 nm). That the first band (*i.e.*, 334 mμ) is not of crystal field nature, as has been suggested in analogous compounds [13, 7], is confirmed by observation of weaker, albeit unresolved, band or bands in the region 525–600 nm (estimated $\epsilon \approx 100$) for ~ 10^{-3} *M* concentration. Since $AsPh_3$ is lower than PPh_3 in the Spectrochemical Series, its crystal field bands are expected at lower energy (assuming analogous solution structures).

From lower melting point, limited stability in solution, and ease of $AsPh_3$ displacement by the phosphorus ligands: PPh_3, $P(OMe)_3$, and $P(OPh)_3$; it may be concluded that $[Co(CNPh)_3(AsPh_3)_2]ClO_4$ is a less stable complex than $[Co(CNPh)_3(PPh_3)_2]ClO_4$. This behavior is also not unexpected.

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