Available online at www.sciencedirect.com

SCIENCE DIRECT®

Inorganica Chimica Acta 359 (2006) 1041–1049

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Diphosphine substitution in pentakis(arylisocyanide)cobalt(I) complexes; ^{31}P NMR, cyclic voltammetric and ESI mass spectrometry studies

F. Foster Mbaiwa *, C.A.L. Becker

Department of Chemistry, University of Botswana, Private Bag 0022, Gaborone, Botswana

Received 10 March 2005; received in revised form 14 November 2005; accepted 14 November 2005
Available online 20 December 2005

Abstract

Five new complexes of the type $[Co(CNC_6H_3iPr_2\text{-}2,6)_4PPh_2\text{-}R'\text{-}PPh_2]X$, X = BF_4, ClO_4; R′ =–$(CH_2)_2$– (**1**), –$(CH_2)_3$– (**2**), –CH=CH-*trans* (**3**), –C≡C– (**4**) and –C_6H_4-*p* (**5**); and two new bimetallic complexes, $[\{Co(CNC_6H_3iPr_2\text{-}2,6)_4\}_2(\mu\text{-}PPh_2(CH_2)_3PPh_2)](ClO_4)_2$ (**6**) and $[\{Co(CNC_6H_3iPr_2\text{-}2,6)_4\}_2(\mu\text{-}PPh_2C_6H_4PPh_2\text{-}p)](ClO_4)_2$ (**7**), have been synthesized and characterized by various spectroscopic methods.Known monometallic and bimetallic complexes bearing the ligand $CNC_6H_3Et_2$-2,6 instead of $CNC_6H_3iPr_2$-2,6 have been included in the ^{31}P NMR, cyclic voltammetric and mass spectrometry studies.Comparison of the $CNC_6H_3iPr_2$-2,6 with the $CNC_6H_3Et_2$-2,6 complexes shows that the increased steric bulkiness of the former makes it more suitable for synthesis of the monometallic complexes, whilst the $CNC_6H_3Et_2$-2,6 is more apt to give bimetallic complexes.Thus, the two arylisocyanides are complementary with respect to synthesis of the monometallic and bimetallic complexes.The ^{31}P NMR indicates that the diphosphines in monometallic complexes behave as non-fluxional, monodentate ligands at ambient temperature, with ^{31}P–^{31}P coupling shown for the $PPh_2CH_2PPh_2$, $PPh_2(CH_2)_2PPh_2$ and $PPh_2C{\equiv}CPPh_2$ ligands. Cyclic voltammetry fails to show electronic communication in the bimetallic complexes, and mass spectrometry indicates significantly greater stability for fragments containing potentially chelating diphosphines as compared to diphosphines that cannot chelate.

Keywords: Arylisocyanides; Diphosphines; Ligand substitution; ^{31}P NMR; Cyclic voltammetry

1. Introduction

The combination of tertiary phosphine and organoisocyanide ligands in the synthesis of metal complexes is significant in that ligand modification can easily be done to achieve desired stereoelectronic properties. These ligand properties are important in most catalytic systems, e.g., in hydroformylation the selectivity has been found to depend on the cone angle of the diphosphine ligand [1].

Previous investigations of bidentate phosphine substitution in $[Co(CNC_6H_3Et_2\text{-}2,6)_5]BF_4$ lead to monosubstituted complexes of the types $[Co(CNC_6H_3Et_2\text{-}2,6)_4(L\text{–}L)]BF_4$ [2] and $[(2,6\text{-}Et_2C_6H_3NC)_4CoL\text{–}LCo(CNC_6H_3Et_2\text{-}2,6)_4](BF_4)_2$ [3], where L–L = $Ph_2P(CH_2)_nPPh_2$, $n = 1$–4; $Ph_2PC_6H_4PPh_2$-*p*, $Ph_2PCH{=}CHPPh_2$-*trans*, $Ph_2PC{\equiv}CP\ Ph_2$. Despite some of these diphosphines having the ability of chelate, no chelate compound was observed. Monometallic or bimetallic product was obtained depending primarily on whether the diphosphine or the cobalt(I) complex was in excess. ^{31}P NMR, cyclic voltammetry, and mass spectrometry data were not available for these complexes. In this paper, monometallic and bimetallic complexes of the types $[Co(CNR)_4(L\text{–}L)]X$ and $[\{Co(CNR)_4\}_2(\mu\text{-}L\text{–}L)]X_2$, R = 2,6-$iPr_2C_6H_3NC$, X = ClO_4, BF_4, have been reported. Syntheses and properties for the complexes containing 2,6-$iPr_2C_6H_3NC$ ligands have been compared and contrasted to the complexes containing 2,6-$Et_2C_6H_3NC$ ligands, the efficacy of the ^{31}P NMR and ESI-MS in

---

* Corresponding author. Tel.: +267 717 33909; fax: +267 355 2836.
E-mail addresses: mbaiwaf@mopipi.ub.bw (F.F. Mbaiwa), Beckerca@mopipi.ub.bw (C.A.L. Becker).

0020-1693/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2005.11.006

characterization of these types of compounds is demonstrated, and the possibility of electronic communication between the two cobalt centres in the bimetallic complexes is investigated using cyclic voltammetry.

2. Experimental

2.1. Materials and methods

$PPh_2CH_2PPh_2$ (dppm), $PPh_2CH_2CH_2PPh_2$ (diphos), $PPh_2CH_2CH_2CH_2PPh_2$ (dppp), $PPh_2CH{=}CHPPh_2$-*trans* (*trans*-dppe), $PPh_2C{\equiv}CPPh_2$ (dppa) and $PPh_2C_6H_4PPh_2$-*p* (*p*-dppb) were supplied by Strem Chemicals, Inc. and used without further purification. Tetra-*n*-butylammonium perchlorate (electrochemical grade) was supplied by Fluka. $[Co(CNC_6H_3iPr_2\text{-}2,6)_5]X$ and $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X$, $X = ClO_4$ or BF_4, were synthesized as previously reported [4,5]. NMR measurements were performed on a Bruker Avance DPX 300 spectrometer. Chemical shift standards were internal tetramethylsilane for ^1H and external 85% H_3PO_4 for ^{31}P. The solvent was $CDCl_3$. Elemental analyses were carried out on a Vario EL CHNOS Elemental analyzer. For cyclic voltammetry ~1.0 mM solutions of the compounds were prepared in dichloromethane containing 0.05 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte. Cyclic voltammetry measurements were performed using a Metrohm 757 VA Computrace system with a three-electrode compartment cell. The working and auxiliary electrodes were both made of glassy carbon. The reference electrode was a double junction Ag/AgCl system. The voltammograms were recorded in the potential range −1.0 to 1.0 V vs. Ag/AgCl at various scan rates ranging from 0.05 to 0.25 $V\,s^{-1}$. Nitrogen gas was bubbled through each solution for 500 s prior to each run. Infrared spectra were measured in the 4000–400 cm^{-1} range with a Spectrum 2000 Perkin–Elmer FT-IR spectrometer using Nujol mull and in solutions of spectro-grade CH_2Cl_2, CH_3NO_2 and CF_3CH_2OH. Electronic spectra were recorded using a Shimadzu UV-2401 PC spectrometer using MeCN, CF_3CH_2OH and CH_2Cl_2 as solvents. Mass spectrometry data were obtained using a Finnigan LCQ deca ion trap quadrupole mass spectrometer at atmospheric pressure and capillary temperature of 300 °C. The solvent used was CH_2Cl_2.

2.2. Synthesis of the complexes

2.2.1. $[Co(CNC_6H_3iPr_2\text{-}2,6)_4PPh_2CH_2CH_2PPh_2]ClO_4 \cdot 1/2\text{-}CH_2Cl_2$ (1)

To a solution of $PPh_2(CH_2)_2PPh_2$ (293 mg (0.74 mmol) dissolved in 3.0 mL of CH_2Cl_2) was added, with continued stirring, 322 mg (0.29 mmol) of $[Co(CNC_6H_3iPr_2\text{-}2,6)_5]ClO_4$ as solid. The reaction mixture was then allowed to stand at room temperature for 50 min. The title compound was then precipitated out by slow addition of diethyl ether. Crystals first appeared after 10 mL of diethyl ether was added. Further 10 mL of diethyl ether was added to allow the complete crystallization of **1**. Cooling in ice for 10 min and filtering afforded yellow powdery material (291 mg), which was dissolved in CH_2Cl_2 (2 mL) and recrystallized by addition of 10 mL of diethyl ether, yielding 235 mg of pure $[Co(CNC_6H_3iPr_2\text{-}2,6)_4PPh_2CH_2CH_2PPh_2]ClO_4 \cdot 1/2\text{-}CH_2Cl_2$. Yield: 61%.

2.2.2. $[\{Co(CNC_6H_3iPr_2\text{-}2,6)_4\}_2(\mu\text{-}PPh_2(CH_2)_3PPh_2)](ClO_4)_2$ (6)

$[Co(CNC_6H_3iPr_2\text{-}2,6)_5]ClO_4$ (700 mg, 0.64 mmol) was added as solid to a stirred solution of $PPh_2(CH_2)_3PPh_2$ (132 mg (0.32 mmol) dissolved in 2 mL of CH_2Cl_2). The reaction mixture was then allowed to react for 1 h 45 min. Drop-wise addition of diethyl ether (20 mL) with careful sweeping of the walls of the reaction vessel with a metal spatula resulted in the formation of yellow micro crystals. The mixture was cooled in ice for 30 min, filtered and washed with 1 mL of diethyl ether. The crude product (561 mg) was dissolved in CH_2Cl_2 (2 mL) and recrystallized by slow and careful addition of diethyl ether (40 mL) yielding 316 mg of the title compound. Yield: 44%.

The compounds $[Co(CNC_6H_3iPr_2\text{-}2,6)_4PPh_2(CH_2)_3PPh_2]ClO_4 \cdot 1CH_2Cl_2$ (**2**), $[Co(CNC_6H_3iPr_2\text{-}2,6)_4(PPh_2CH{=}CHPPh_2\text{-}trans)]ClO_4 \cdot 1CH_2Cl_2$ (**3**) and $[Co(CNC_6H_3iPr_2\text{-}2,6)_4(PPh_2C_6H_4PPh_2\text{-}p)]ClO_4 \cdot 1CH_2Cl_2$ (**5**) were synthesized according to the synthesis of $[Co(CNC_6H_3iPr_2\text{-}2,6)_4PPh_2CH_2CH_2PPh_2]ClO_4 \cdot 1/2CH_2Cl_2$. The synthesis of $[\{Co(CNC_6H_3iPr_2\text{-}2,6)_4\}_2(\mu\text{-}PPh_2C_6H_4PPh_2\text{-}p)](ClO_4)_2$ (**7**) resembles that of $[\{Co(CNC_6H_3iPr_2\text{-}2,6)_4\}_2(\mu\text{-}PPh_2(CH_2)_3PPh_2)](ClO_4)_2$. The previously reported monometallic compounds [2] of the type $[Co(CNC_6H_3Et_2\text{-}2,6)_4PPh_2\text{-}R'\text{-}PPh_2]X$; $X = BF_4/ClO_4$, $R' = {-}CH_2{-}$ (**8**), $-(CH_2)_2-$ (**9**), $-(CH_2)_3-$ (**10**), or *trans*-CH=CH– (**11**), and bimetallic compounds [3] of the type $[\{Co(CNC_6H_3Et_2\text{-}2,6)_4\}_2(\mu\text{-}PPh_2\text{-}R'\text{-}PPh_2)]X_2$; $R' = -(CH_2)_2-$ (**12**), $-C{\equiv}C-$ (**13**) and $p\text{-}C_6H_4-$ (**14**), have also been included in this work.

3. Results and discussion

Even though excess tertiary diphosphine ligand was used (i.e., Co:P mol ratio of 1:2.5–3.0) in synthesis of the monometallic complexes, $[Co(CNC_6H_3iPr_2\text{-}2,6)_5]X$, analogous to $[Co(CNC_6H_3Et_2\text{-}2,6)_5]X$ [6], clearly shows preference for monosubstitution over disubstitution. This follows the trend previously observed for triarylphosphine substitution reactions in pentakis(arylisocyanide)cobalt(I) complexes. Reactions of excess PPh_3 with $[Co(CNR)_5]X$, R = Ph, C_6H_4Me-*p*, C_6H_4Me-*o*, C_6H_4F-*p*, C_6H_4Cl-*p*, C_6H_4Br-*p*, C_6H_4I-*p*; clearly favoured disubstituted products, i.e., $[Co(CNR)_3(PPh_3)_2]X$; while reactions with $[Co(CNR)_5]X$, $R = 2,6\text{-}Me_2C_6H_3$, $2,4,6\text{-}Me_3C_6H_2$, $2,6\text{-}Et_2C_6H_3$ favoured monosubstituted products, $[Co(CNR)_4PPh_3]X$ [6]. Preference for monosubstitution over disubstitution was seen to roughly parallel the apparent steric hindrance of the arylisocyanide: $p\text{-}MeC_6H_4NC < o\text{-}Me\ C_6H_4NC \ll 2,4,6\text{-}Me_3C_6H_2NC \leqslant 2,6\text{-}Me_2C_6H_3NC < 2,6\text{-}Et_2C_6H_3NC$ [7]. $[Co(CNC_6H_3Et_2\text{-}2,6)_5]ClO_4$ also indicated monosubstitution