ELSEVIER

Inorganica Chimica Acta 230 (1995) 231–233

Inorganica Chimica Acta

Note

Convenient preparation of $[CuX(PCy_3)_2]$ (X = Br, I, SCN, N_3) complexes. X-ray crystal structure of $[Cu(N_3)(PCy_3)_2]$ (Cy = *cyclo*-C_6H_{11})

Jason Green, Ekkehard Sinn, Simon Woodward *

School of Chemistry, University of Hull, Kingston-upon-Hull HU6 7RX, UK

Received 24 May 1994; revised 20 July 1994

Abstract

The labile cations $[Cu(F\text{-}BF_3)(PCy_3)_2]$ and $[Cu(OTf)(PCy_3)_2]$ are versatile precursors for the formation of $[Cu(X)(PCy_3)_2]$ (X = Br, I, SCN, N_3) complexes by metathesis with NaX. The azide $[Cu(N_3)(PCy_3)_2]$ is triclinic, space group $P\bar{1}$, $a = 9.755(4)$, $b = 22.78(1)$, $c = 9.284(6)$ Å, $\alpha = 96.76(3)$, $\beta = 115.36(3)$, $\gamma = 94.20(5)°$, $Z = 2$.

Keywords: Crystal structures; Copper complexes; Azido complexes; Tertiary phosphine complexes

1. Introduction

We are interested in the structural and catalytic properties of $[Cu(X)(PCy_3)_2]$ complexes [1]. Despite their simple nature no good routes to these new molecules have been reported. Classical approaches to copper(I) phosphine species involve the reduction of copper(II) sources by phosphine ligands with concomitant oxidation of some ligand to phosphine oxide [2]. We had a need for samples guaranteed free of phosphine oxide contamination necessitating an alternative approach to the syntheses of these species.

2. Results and discussion

Reaction of aqueous NaX solutions with dichloromethane solutions of either $[Cu(F\text{-}BF_3)(PCy_3)_2]$ (**1**) or $[Cu(OTf)(PCy_3)_2]$ (**2**) (OTf = O_3SCF_3) lead to the formation of $[Cu(X)(PCy_3)_2]$ in good yields. The bromide **3**, iodide **4**, thiocyanate **5**, and azide **6** are given as representative examples. The reaction is most conveniently carried out in a nitrogen-flushed separatory funnel. The precursor triflate **2**, if used, is easily prepared from $[Cu(NCMe)_4]OTf$ and PCy_3.

The compounds **3**–**6** are isolated in analytical purity but may be readily crystallised from diethyl ether containing traces of dichloromethane. In particular the azide $[Cu(N_3)(PCy_3)_2]$ (**6**) is highly crystalline. Although, azide is a rather common ligand encountered in copper(II) chemistry [3] crystallographically characterised copper(I) coordination geometries are apparently limited to dimeric $[Cu(N_3)(PPh_3)_2]_2$ (**7**) [4]. It is therefore of interest to compare the crystal structures of **6** and **7**.

An ORTEP view of $[Cu(N_3)(PCy_3)_2]$ (**6**) is shown in Fig. 1, while final fractional atomic coordinates and selected bond lengths and angles appear in Tables 1 and 2. The molecule is three-coordinate and mononuclear with a P–Cu–P angle of 134.65(7)°, greater than those in **7** (120.8(1), 122.3(1)°). All of these observations are undoubtedly linked to the larger cone angle of PCy_3 ($\theta_{cone} = 170°$) compared to PPh_3 ($\theta_{cone} = 145°$). The azide is more tightly bound in **6** (Cu–N 1.948(5) Å) than those in **7** (Cu–N 2.085(10), 2.102(10), 2.109(11), 2.116(10) Å). The change in coordination geometry from **7** to **6** also results in an opening of the Cu–N–N angle from 122.3° (average for **7**) to 144.4(5)° in **6**, however, the bond lengths and angles within the coordinated N_3 unit are essentially identical in **6** and **7**.

---

* Corresponding author.

SSDI 0020-1693(94)04296-8

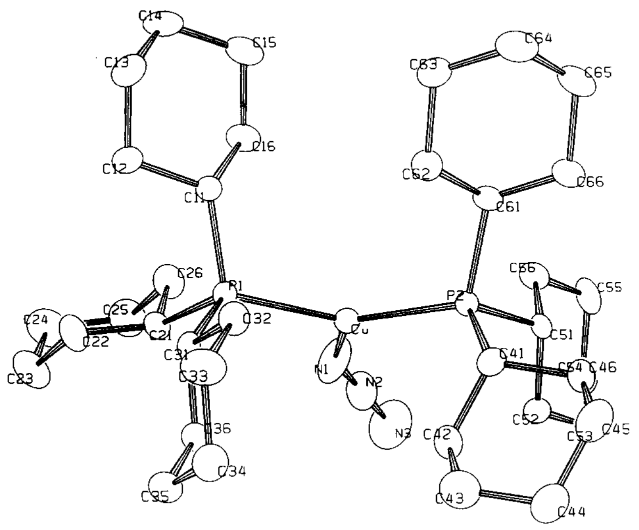

Fig. 1. An ORTEP view of $[Cu(N_3)(PCy_3)_2]$ (**6**).

Table 1

Final atomic coordinates for $[Cu(N_3)(PCy_3)_2]$ (**6**)

Atom	*x*	*y*	*z*
Cu	0.15214(7)	0.24829(3)	−0.06189(7)
P(1)	0.2236(1)	0.16179(7)	−0.1411(1)
P(2)	0.1066(2)	0.33498(7)	−0.1579(2)
N(1)	0.1421(7)	0.2391(3)	0.1395(7)
N(2)	0.0980(6)	0.2571(3)	0.2263(6)
N(3)	0.0450(8)	0.2758(3)	0.3137(7)
C(11)	0.4061(5)	0.1732(3)	−0.1572(5)
C(12)	0.4715(6)	0.1192(3)	−0.2005(7)
C(13)	0.6104(7)	0.1389(3)	−0.2301(7)
C(14)	0.7323(6)	0.1786(3)	−0.0834(7)
C(15)	0.6712(6)	0.2340(3)	−0.0369(7)
C(16)	0.5306(6)	0.2155(3)	−0.0100(6)
C(21)	0.2376(6)	0.1082(3)	0.0010(6)
C(22)	0.2425(7)	0.0436(3)	−0.0496(6)
C(23)	0.2316(7)	0.0045(3)	0.0739(8)
C(24)	0.3512(8)	0.0286(4)	0.2429(8)
C(25)	0.3509(7)	0.0938(4)	0.2912(7)
C(26)	0.3641(6)	0.1318(3)	0.1704(6)
C(31)	0.0895(5)	0.1182(2)	−0.3414(5)
C(32)	0.0778(6)	0.1516(3)	−0.4788(6)
C(33)	−0.0373(7)	0.1154(3)	−0.6442(6)
C(34)	−0.1933(7)	0.0999(3)	−0.6493(7)
C(35)	−0.1824(6)	0.0670(3)	−0.5131(7)
C(36)	−0.0679(6)	0.1028(3)	−0.3482(6)
C(41)	−0.0585(6)	0.3270(3)	−0.3610(6)
C(42)	−0.1830(6)	0.2782(3)	−0.3852(6)
C(43)	−0.3078(7)	0.2666(3)	−0.5614(7)
C(44)	−0.3752(7)	0.3215(4)	−0.6137(7)
C(45)	−0.2511(8)	0.3701(3)	−0.5888(7)
C(46)	−0.1289(6)	0.3834(3)	−0.4120(7)
C(51)	0.0733(5)	0.3936(2)	−0.0264(6)
C(52)	−0.0695(6)	0.3736(3)	−0.0030(6)
C(53)	−0.0951(7)	0.4194(3)	0.1107(7)
C(54)	0.0439(8)	0.4363(3)	0.2720(7)
C(55)	0.1854(7)	0.4573(3)	0.2509(7)
C(56)	0.2139(6)	0.4116(3)	0.1391(6)
C(61)	0.2745(6)	0.3715(3)	−0.1766(6)
C(62)	0.3205(7)	0.3277(3)	−0.2813(8)
C(63)	0.4750(7)	0.3527(3)	−0.2751(8)
C(64)	0.4697(8)	0.4122(4)	−0.324(1)
C(65)	0.4250(8)	0.4556(4)	−0.223(1)
C(66)	0.2717(7)	0.4308(3)	−0.2232(8)

Table 2

Selected bond distances (Å) and angles (°) for $[Cu(N_3)(PCy_3)_2]$ (**6**)

Cu–P(1)	2.282(3)	Cu–P(2)	2.257(3)
Cu–N(1)	1.948(5)	P(1)–C(11)	1.852(5)
P(1)–C(21)	1.871(6)	P(1)–C(31)	1.856(5)
P(2)–C(41)	1.859(5)	P(2)–C(51)	1.843(5)
P(2)–C(61)	1.866(6)	N(1)–N(2)	1.117(6)
N(2)–N(3)	1.190(6)		
P(1)–Cu–P(2)	134.65(7)	P(1)–Cu–N(1)	105.8(2)
P(2)–Cu–N(1)	119.5(2)	Cu–N(1)–N(2)	144.4(5)
N(1)–N(2)–N(3)	177.2(8)		

3. Experimental

3.1. General

All manipulations, except where noted otherwise, were carried out under a nitrogen atmosphere using standard Schlenk techniques. Dichloromethane was distilled from CaH_2 immediately prior to use; hexane, light petroleum (b.p. 40–60 °C) and Et_2O were dried over sodium wire. All other reagents were used as supplied. IR spectra were recorded using a Perkin-Elmer 983G instrument. Proton, ^{13}C and ^{31}P NMR spectra were recorded on a Jeol-270 spectrometer. Mass spectra were obtained on Finnigan 1020 (electron impact ionisation, EI) or VG-ZAB (fast atom bombardment ionisation, FAB) machines. The complexes $[Cu(F\text{-}BF_3)(PCy_3)_3]$ (**1**) and $[Cu(NCMe)_4]OTf$ were prepared as previously described [1].

3.2. Preparation of [Cu(OTf)(PCy₃)₂] (2)

Solid PCy_3 (0.30 g, 1.07 mol) was added to a suspension of $[Cu(NCMe)_4]OTf$ (0.18 g, 0.48 mmol) in CH_2Cl_2 (15 cm^3) at room temperature. After 2 h the resulting colourless solution was concentrated to a minimal volume and crystallised by the addition of ether and cooling, resulting in two crops of colourless crystalline material 0.20 g (53%). M.p. 187–188 °C. *Anal.* Found: C, 57.45; H, 8.32. Calc. for $C_{37}H_{66}CuF_3O_3P_2S$: C, 57.45; H, 8.60%. ^1H NMR (270 MHz, $CDCl_3$): δ_H 1.15–1.53 (30H, m, Cy), 1.61–2.10 (36H, m, Cy). ^{31}P NMR (109.3 MHz, $CDCl_3$): δ_P 15.6 [PCy_3]. ^{13}C NMR (67.8 MHz, $CDCl_3$): δ_C 26.2, 27.3, 30.8 (CH_2), 32.3 (t, $J(PC) = 8.5$ Hz, CH), 120.3 (q, $J(CF) = 326$ Hz, CF_3). IR (KBr disc): 2932s, 2854s (CH), 1449s, 1349w, 1307s, 1280m, 1235s, 1218s, 1167s, 1027s, 855m, 635s, 514m cm^{-1}. MS (EI): 280 $[PCy_3]^+$.

3.3. Preparation of [Cu(X)(PCy₃)₂], X = Br (3), I (4), SCN (5), N₃ (6)

A solution of either $[Cu(F\text{-}BF_3)(PCy_3)_2]$ (**1**) (0.20 g, 0.28 mmol) or $[Cu(OTf)(PCy_3)_2]$ (**2**) in CH_2Cl_2 (5 cm^3)

was shaken vigorously with a concentrated solution of NaX (0.56 mmol) in H_2O (2 cm^3) in a small nitrogen-flushed separatory funnel. The dichloromethane layer was separated, concentrated to a minimal volume and the product crystallised by the addition of Et_2O and cooling yielding the appropriate complex.

[Cu(Br)(PCy$_3$)$_2$] (3). Yield 0.14 g, 69%. M.p. 190–192 °C. *Anal.* Found: C, 61.12; H, 9.51. Calc. for $C_{36}H_{66}BrCuP_2$: C, 61.39; H, 9.44%. ^1H NMR (270 MHz, $CDCl_3$): δ_H 2.02–2.18 (66H, m, Cy). ^{31}P NMR (109.3 MHz, $CDCl_3$): δ_P 11.5 (PCy_3). IR (KBr disc) 2932s, 2858s (CH), 1454s, 1350w, 1274w, 1175w, 1111w, 1087w, 1048w, 1007m, 890m, 852m cm^{-1}. MS (EI): 424 $[CuBr(PCy_3)]^+$.

[Cu(I)(PCy$_3$)$_2$] (4). Yield 0.15 g, 72%. M.p. 176–177 °C. *Anal.* Found: C, 57.29; H, 8.64. Calc. for $C_{36}H_{66}CuIP_2$: C, 57.55; H, 8.85%. ^1H NMR (270 MHz, $CDCl_3$): δ_H 2.02–2.18 (66H, m, Cy). ^{31}P NMR (109.3 MHz, $CDCl_3$): δ_P 11.5 (PCy_3). IR (KBr disc): 2928s, 2860s (CH), 1445s, 1333w, 1270w, 1185m, 1112m, 1072w, 1041w, 1001m, 890m, 852m cm^{-1}. MS (EI): 470 $[CuI(PCy_3)]^+$.

[Cu(SCN)(PCy$_3$)$_2$] (5). Yield 0.17 g, 88%. M.p. 126–127 °C. *Anal.* Found: C, 64.91; H, 9.88; N, 1.96. Calc. for $C_{37}H_{66}CuNSP_2$: C, 65.11; H, 9.75; N, 2.05%. ^1H NMR (270 MHz, $CDCl_3$): δ_H 2.02–2.18 (66H, m, Cy). ^{31}P NMR (109.3 MHz, $CDCl_3$): δ_P 11.5 (PCy_3). IR (KBr disc): 2912s, 2858s (CH), 2660m, 2080s, 1449s, 1360m, 1302m, 1277m, 1208m, 1187m, 1121m, 1076m, 1055m, 1045m, 1005s, 918m, 890s, 852s (SCN), 760m, 749m, 730m cm^{-1}. MS (EI): 343 $[Cu(PCy_3)]^+$.

[Cu(N$_3$)(PCy$_3$)$_2$] (6). Yield 0.15 g, 78%. M.p. 160–161 °C. *Anal.* Found: C, 64.82; H, 10.10; N, 6.22. Calc. for $C_{36}H_{66}CuN_3P_2$: C, 64.88; H, 9.98; N, 6.30%. ^1H NMR (270 MHz, $CDCl_3$): δ_H 2.02–2.18 (66H, m, Cy). ^{31}P NMR (109.25 MHz, $CDCl_3$): δ_P 11.5 (PCy_3). IR (KBr disc): 2930s, 2860s (CH), 2040s (N_3), 1968sh m, 1450s, 1388w, 1268w, 1181m, 1115m, 1075w, 1042w, 1008m, 889m, 852m cm^{-1}. MS (FAB): 728 $[(Cy_3P)Cu(\mu\text{-}N_3)Cu(PCy_3)]^+$, 623 $[Cu(PCy_3)_2]^+$.

3.4. *Crystal data for [Cu(N$_3$)(PCy$_3$)$_2$] (6)*

$C_{36}H_{66}CuN_3P_2$, $M = 666.43$, triclinic, space group $P\bar{1}$, $a = 9.755(4)$, $b = 22.78(1)$, $c = 9.284(6)$ Å, $\alpha = 96.76(3)$, $\beta = 115.36(3)$; $\gamma = 94.20(5)$°, $U = 1833$ Å^3, $D_c = 1.207$ g cm^{-3}, $Z = 2$, $F(000) = 724$. A colourless crystal of size 0.35×0.35×0.05 mm, μ(Mo Kα) = 7.1 cm^{-1} was used in the data collection.

Data were collected at 23 °C on a Rigaku AFC6S four circle diffractometer, θ range 34.3–39.4°, with scan width A+B tan θ, A = 0.65, B = 0.35°. Of the 6883 reflections collected 4267 were unique and observed ($>3\sigma$). The data were corrected for Lorentz–polarisation effects and for absorption.

Computations were carried out using the data with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics [5]. Lorentz and polarisation effects and effects for absorption [6] were applied. The position of the metal atom was determined from a Patterson map. Other atoms were located from Fourier difference syntheses. The refinement and final full-matrix least-squares refinement was carried out using the TEXRAY program set [7]. Full-matrix least-squares refinement was based on F. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where: $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + 0.03F_o^2)^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarisation factor. Atomic scattering factors for non-hydrogen atoms were taken from Ref. [8] and those for hydrogen from Ref. [9]. The effects of anomalous dispersion were included using values for $\Delta f'$ and $\Delta f''$ from Ref. [10]. The model converged with $R = 5.8\%$, $R_w = 5.4\%$ ($GOF = 2.56$).

Acknowledgements

We thank the EPSRC for a studentship to J.G. and for their mass spectroscopy service. We are grateful to Dr Simon Kitchen (BP Chemicals Ltd.) for a contribution.

References

[1] J. Green, E. Sinn, S. Woodward and R. Butcher, *Polyhedron, 12* (1993) 991.

[2] B.J. Hathaway, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 5, Pergamon, Oxford, 1987, p. 533.

[3] K. Vrieze and G. Van Koten, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 2, Pergamon, Oxford, 1987, p. 189.

[4] R.F. Ziolo, A.P. Gaughan, Z. Dori, C.G. Pierpont and R. Eisenberg, *Inorg. Chem., 10* (1971) 1289.

[5] P.W.P. Corfield, R.J. Doedens and J.A. Ibers, *Inorg. Chem., 6* (1967) 197.

[6] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

[7] *TEXRAY,* structure analysis package, Molecular Structure Corporation, Houston, TX, 1985.

[8] D.T. Cromer and J.T. Waber, *Acta Crystallogr., 18* (1965) 511.

[9] R.F. Stewart and E.R. Davidson, *J. Chem. Phys., 45* (1965) 3175.

[10] D.T. Cromer, *Acta Crystallogr., 18* (1965) 17.