Inorganica Chimica Acta, 207 (1993) 59–63

Reactivity of copper metal vapours with substituted bromobenzenes. Formation and molecular structure of $Cu(PMe_3)_3Br$

J. C. Negrel*, M. Gony, M. Chanon
URA 1411, Université Aix-Marseille III, 13013 Marseille (France)

and R. Lai*
E.N.S.S.P.I.C.A.M., URA 1410, Université Aix-Marseille III, 13013 Marseille (France)

(Received September 24, 1992; revised November 30, 1992)

Abstract

Substituted bromobenzenes YArBr (Y = *o*-NH_2, *o*-OMe or *p*-OMe) have been allowed to react with copper vapours at −108 °C in THF solutions with a rotary metal atom apparatus. Addition of PMe_3 or t-BuNC at different temperatures to these solutions led to the isolation of $Cu(PMe_3)_3Br$ (**1**) and $(t\text{-}BuNC)_4CuBr$ (**2**), respectively. The crystal structure of **1** has been determined by X-ray diffraction. Crystals of **1** belong to the cubic space group $Pa\bar{3}$ with $Z = 8$, $a = 15.7451$ Å, $D_c = 1.26$ g cm^{-3}, $R = 0.0395$. Analyses of the THF solutions showed the presence of reduction and coupling products of the aromatic substrates together with a coupling product arising from the bromoarenes and THF. These results suggest that the reactions between haloarenes and copper vapours proceed through dehalogenation of the haloarenes with formation of copper bromide and of aryl radicals which are responsible for the observed organic products.

Introduction

Metal vapour chemistry has, so far, mainly been used to obtain new organometallic structures or to perform reactions otherwise impossible under classical conditions [1].

A profitable area of research has been the reactions of atoms of the nickel triad with organic halides. Often, the products obtained during these reactions are unstable and lead to decomposition products [2a, b]. We have recently shown that copper vapours react with substituted bromobenzenes to yield coupling and reduction products [3a, c]. Together with biaryls other mixed coupling compounds were detected which arose from the aromatic substrates and the solvents used (methylcyclohexane or THF).

This type of reaction is comparable to the heterogeneous Ullman reaction used for the production of biaryls with copper powder [4]. Coupling of halogenobenzenes can also be achieved with different nickel systems [5a–c] or with nickel vapours [3d].

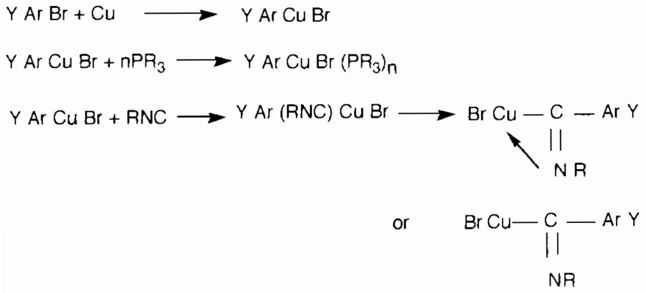
The mechanism of formation of biaryls and of the other products formed in these reactions is still a matter of controversy. Whatever the type of system used, homogeneous or heterogeneous, and the nature of the metal, nickel or copper, an oxidative addition/disproportionation/reductive elimination process has been proposed as operative for the production of coupling and reduction products [6a–e]. These hypotheses find some support from the results obtained by Tsou and Kochi with nickel complexes [5b]. Indeed, arylnickel(II) halide phosphine complexes have been synthesized and found to yield biaryls upon treatment with aryl halides. These results seemed to cast doubt on the presence of free radicals as possible intermediates in this system. However, in cocondensation conditions at −196 °C, a free radical pathway, associated with metal clustering, was assumed in order to explain the formation of reduction products [7].

We wish to report here our results of a study aimed at showing some evidence of such oxidative addition products in the copper vapour reactions with substituted bromobenzenes, performed by the 'in solution' technique [8] at −108 °C. Because the isolation of such species is rather uncertain due to their instability, we added ligands such as phosphines or isonitriles which could lead to the isolation of ligand-stabilized intermediates.

---

*Authors to whom correspondence should be addressed.

0020-1693/93/$6.00



Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 X spectrometer; IR spectra on an FT-IR Nicolet MX-S instrument. GC/MS were carried out on a Ribermag R 10-10C apparatus and GC/FT-IR on a Nicolet 20 SXB bench/Carlo Erba HRGC 5300 Mega Serie gas chromatograph. The GC analyses were performed on a Shimadzu model GC-14A flame ionisation gas chromatograph: carrier gas; N_2; column, OV101 25 m. 2,6-Dimethylnaphthalene was used as internal standard.

Elemental analyses were carried out by the Service Central d'Analyses CNRS.

All manipulations were conducted under purified N_2 or Ar by standard Schlenk techniques. THF, pentane and diethyl ether were distilled under nitrogen from sodium benzophenone ketyl. Trimethylphosphine [9] and t-BuNC [10] were prepared according to literature methods.

For the solution reactions we used a small-sized rotary metal atom reactor according to the principle of the Green apparatus [3b]. This new home-made 'bench-top type' reactor derived from our first machine [3c], was equipped with a three-liter round-bottom flask. A water-cooled shielding stopped the radiant heat emitted by the crucible in five directions; the temperature of the solution inside the reactor was continuously monitored. The reactor was evacuated to approximately 7×10^{-4} Torr and maintained at −108 °C with a methylcyclohexane bath cooled with liquid nitrogen, the flask was rotated at 20 rpm and a solution (previously degassed by three freeze–pump–thaw cycles) of 3 g of aryl halide in 200 ml THF was introduced into the reactor. In a typical experiment, 1 g of copper (99.99% Cerac) was vaporized within one hour from an alumina-coated crucible (Sylvania).

A new liquid-film cooling system of the reactor enabled us to largely reduce pyrolysis from the source.

At the end of the reaction of copper vapors with the liquid film, the reactor was isolated and returned to atmospheric pressure with purified N_2. The reaction mixture was quantitatively recovered with a thermostated flexible transfer-tubing at −100 °C.

X-ray crystallographic measurements

A crystal, obtained from THF/Et_2O at −20 °C, was protected by silicone oil and mounted on an Enraf-Nonius CAD4 diffractometer equipped with a monochromator for Mo Kα radiation ($\lambda = 0.7107$ Å). A total of 518 unique reflections with $I > 3\sigma(I)$ was used in the structure determination. Data were corrected for Lp but not for absorption or secondary extinction. The structure was determined by direct methods (MULTAN) [11] using SDP software [12] and completed by the difference Fourier method. H atoms were introduced at idealized positions in the calculation before the last refinement cycles but not refined. Full least-squares refinements included anisotropic thermal parameters for non-H atoms. A final difference Fourier synthesis did not reveal any peak of density > 0.27 e^{-3}.

Results and discussion

When copper was vaporized into solutions of substituted bromobenzenes YArBr (Y = *o*-NH_2, *o*-OMe or *p*-OMe) at −108 °C in THF, dark green (Y = *o*-OMe), dark red (Y = *p*-OMe) or yellow–green (Y = *o*-NH_2) solutions were obtained within a few minutes. When trimethylphosphine dissolved in THF was then injected into these solutions, at different temperatures (−80, −20 and 15 °C), a colour change occurred rapidly. After workup, whatever the nature of the substituted bromobenzene and the amount of PMe_3 with respect to copper, only one compound could be isolated from the reaction mixtures as a white crystalline solid. On the basis of spectroscopic and analytical data, this compound was identified as $CuBr(PMe_3)_3$ (**1**) (65% yield with respect to PMe_3).

The ^1H and the ^{13}C NMR spectra of **1** displayed a doublet for the methyl group at 1.29 (J(HP) = 6.3 Hz) and 15.0 (J(CP) = 20.3 Hz) ppm, respectively. In the ^{31}P NMR spectrum a sharp singlet appeared at −48.1 ppm (Elimination of paramagnetic impurities has to be made by passing **1** on a silica gel column before running the NMR spectrum.)

An X-ray diffraction study confirmed the structure of **1** and the results of this study are summarized in Tables 1 and 2 and illustrated in Figs. 1 and 2. The angle values at the copper atom indicate that the geometry about the metal is a distorted tetrahedron. As in other complexes of the general formula $CuX(R_3P)_3$, the copper(I)–phosphorus bond distance of 2.240(2) Å is shorter than those found for bulkier and less basic phosphines than PMe_3 [13].

TABLE 1. Crystallographic data for $CuBr(PMe_3)_3$

Formula	$C_9H_{27}BrP_3Cu$
M_r (g)	371.69
Crystal system	cubic
Space group	$Pa\bar{3}$
a (Å)	15.7451
V (Å^3)	3903.3
Z	8
D_{calc} (g/cm^3)	1.26
Crystal size (mm)	0.5×0.4×0.4
μ (cm^{-1})	33.7
Scan mode	θ:2θ
Temperature of measurement (°C)	20
θ_{max} (°)	24
F(0 0 0)	1520
No. reflections measured	3306 (θ_{max}=24°)
No. reflections used	518
No. variables refined	47
R	0.0395
R_w	0.0459

TABLE 2. Bond lengths (Å) and angles (°) for $CuBr(PMe_3)_3$

Cu–Br	2.5044(6)
Cu–P	2.240(2)
P–C(1)	1.817(9)
P–C(2)	1.822(9)
P–C(3)	1.785(9)
Cu–P–C(1)	117.7(3)
Cu–P–C(2)	116.5(3)
Cu–P–C(3)	115.7(3)
C(1)–P–C(2)	101.2(4)
C(1)–P–C(3)	100.3(5)
C(2)–P–C(3)	102.8(5)
P–Cu–Br	103.64(6)
P–Cu–P	114.6(5)

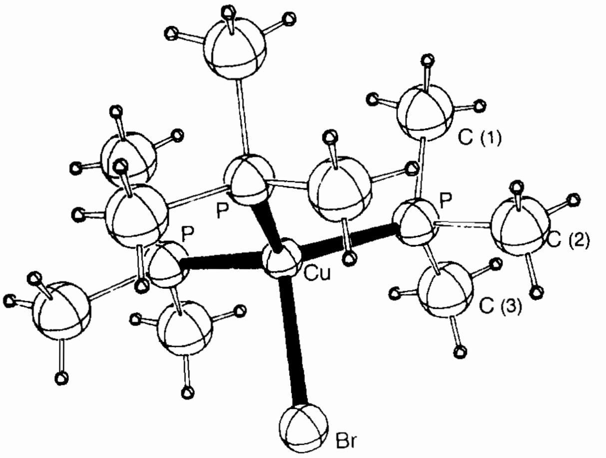


Fig. 1. Molecular structure of $CuBr(PMe_3)_3$.

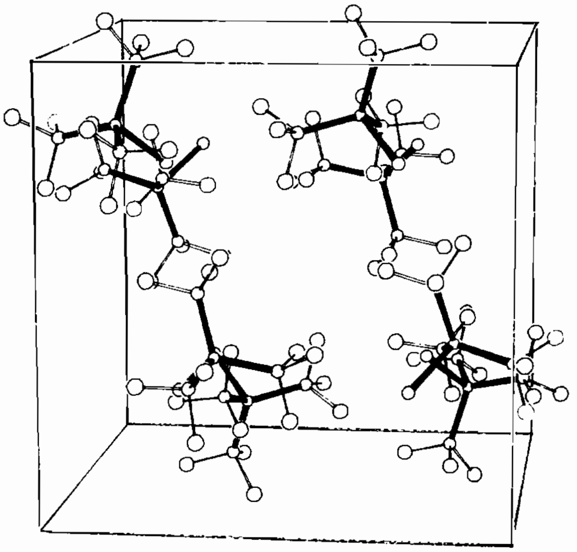


Fig. 2. View of the unit cell of $CuBr(PMe_3)_3$ structure.

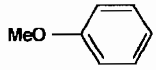
When t-BuNC was allowed to react with THF solutions containing the products formed between copper vapours and substituted bromobenzenes, an even faster reaction than that obtained with PMe_3 occurred. Even at −80 °C an instantaneous colour change of the solution was observed. From the reaction mixture, whatever the starting bromobenzene, a single white crystalline solid was isolated. Using spectroscopic and analytical data it was identified as $[Cu(t\text{-}BuNC)_4]Br$ (**2**). Compound **2** exhibited a singlet at 1.44 ppm in the ^1H NMR spectrum and three signals in the ^{13}C NMR spectrum; two sharp singlets at 30.2 and 56.3 ppm for the tert-butyl group and a broad singlet at 138.9 ppm for the carbon of the isocyanide group*. The stretching band of this group appeared at 2177 cm^{-1} in the IR spectrum.

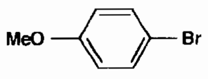
The results clearly show that no products indicative of the formation of oxidative addition compounds between Cu^0 and YArBr, or, species arising from the decomposition of such intermediates, were detected after interaction with PMe_3 or t-BuNC.

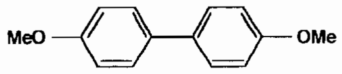
Another interesting observation concerns the composition of the organic products determined by GLC in THF solutions. In the case of *p*-bromoanisole, in the absence or in the presence of PMe_3 or t-BuNC at three different temperatures, the same four products were detected and identified by GC/MS in the case of A (reduction product), B (*p*-bromoanisole) and C (coupling product), and by GC/MS, GC/IR and NMR in the case of D (coupling product between the anisyl group and THF).

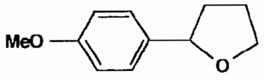
---

*As for **1**, crude $[Cu(t\text{-}BuNC)_4]Br$ was contaminated by trace amounts of paramagnetic impurities which can be discarded by passing **2** through a pad of Celite.

A :


B :


C :


D :


Examination of the data of Table 3 calls for the following comments. The reduction product A predominates and transformation of the aromatic substrate B into A, C and D is rather high compared with experiments run in rigid matrix. Furthermore, it is clear that, whatever the conditions of the reaction between *p*-bromoanisole and copper vapors, there are almost no significant differences in the repartition of the organic products.

The fact that PMe_3 and t-BuNC addition still results in the same products distribution seems to preclude an oxidative addition process. If $ArCuBr(L)_x$ was an intermediate, L should have an effect on decomposition pathways.

One could also argue that under our conditions, even at −108 °C, an oxidative addition step could be operative and lead to the formation of CuBr and phenyl radicals upon decomposition of the unstable oxidative addition products. However, on the basis of analytical data of Table 3, together with the production of **1** and **2** in high yields and of D, a different reaction path has to be envisioned. The first step occurring at low temperature might be the dehalogenation of the haloarene by Cu^0 producing CuBr and phenyl radicals. The formation of **1** and **2** can be rationalized by the reaction of CuBr with PMe_3 and t-BuNC, respectively. Efficient abstraction of halogens by copper atoms has, indeed, been reported by Timms [14a]. It is interesting to point out, that under the conditions used in this work, the reactions with PMe_3 and t-BuNC are much faster than in usual reactions involving CuBr and PR_3 or t-BuNC [15]. An experiment conducted under the same conditions with anisole resulted in the formation of metallic particles and analyses of the reaction mixture showed the absence of any products usually formed with halogenobenzenes. This observation might imply that the initial step of the reaction in solution of copper atoms with the halogenobenzenes could be a complexation of copper with the halogen [14b] rather than a π complexation through the aromatic ring as already proposed for the cocondensation conditions [7].

TABLE 3. GLC analysis of the organic products obtained in the reaction of copper vapours and *p*-bromoanisole

	Temperature (°C)								
	−80			−15			+20		
	a	b	c	a	b	c	a	b	c
A (%)	22.5	31.5	24.3	22.7	24.9	22.2	24.6	28.9	21.0
B (%)	67.5	63.4	68.9	68.1	64.2	67.8	67.4	65.0	67.6
C (%)	6.1	2.5	2.7	5.7	2.2	4.0	4.8	1.9	4.8
D (%)	3.9	2.6	4.1	3.5	4.2	6.0	3.2	4.2	6.6

[a]Without additional ligand (*p*-bromoanisole/Cu = 1.40). [b]PMe_3 (*p*-bromoanisole/Cu = 1.22; PMe_3/Cu = 1.5). [c]t-BuNC (*p*-bromoanisole/Cu = 1.25; t-BuNC/Cu = 1.7).

In solution, more and more data support the concept of size-dependent potential [16a, b]. More specifically, atomic copper has been shown to be a far better reducing agent ($E° = -2.7$ V versus NHE in H_2O) than clusters of Cu or bulk Cu ($E° > 0$ versus NHE in H_2O) [17]. The radical process could be triggered by an outer sphere electron transfer process [18] from copper atoms to the studied substrate.

$$Cu^{\circ} + YArBr \longrightarrow Cu^{I} + YArBr^{\cdot -} \longrightarrow CuBr + YAr^{\cdot}$$

At −108 °C and even below, the phenyl radicals would induce a radical chain process responsible for the production of the different organic products detected in the reaction mixtures. The accompanying formation of D is in agreement with this hypothesis and provides an explanation for the source of hydrogen necessary for the conversion of phenyl radicals into reduction products. Because of the small amount of D with respect to A, it is highly plausible that abstraction of $H^{\cdot}$ from THF leads to other products which are not detected under our experimental conditions. Thus, in these reactions of copper vapors under homogeneous conditions, a free radical process seems to be operative. This is in striking contrast with the lower-energy metal-clustering favorized cocondensation reactions, in which both radical process and oxidative addition pathway are invoked to explain the formation of reduction and coupling products, respectively [7].

Furthermore, a tentative explanation for the difference of reactivity between copper and nickel vapors with halogenobenzenes could lie in the propensity of copper for halogen abstraction in contrast with nickel which preferentially affords oxidative-addition species, owing to ground state electronic configurations (Ni d^8 s^2, Cu d^{10} s^1); this is in agreement with recent work reported by Klabunde *et al.* [19] and Blomberg *et al.* [20].

Supplementary material

Complete X-ray data are available from the authors.

Acknowledgements

We thank Dr M. Pierrot, Dr N. Benali-Cherif and Mr M. Giorgi for the X-ray structure determination.

References

1 (a) P. S. Skell, L. D. Wescott, Jr., J. P. Goldstein and R. R. Engel, *J. Am. Chem. Soc., 87* (1965) 2; (b) M. Moskovits and G. A. Ozin (eds.), *Cryochemistry,* Wiley, New York, 1976; (c) Y. Imizu and K. J. Klabunde, *Inorg. Chem., 23* (1984) 3602; (d) H. Hanai, B. J. Tan and K. J. Klabunde, *Langmuir, 2* (1986) 760.

2 (a) J. R. Blackborow and D. Young, *Metal Vapour Synthesis in Organometallic Chemistry,* Springer, Berlin, 1979; (b) K. J. Klabunde, *Chemistry of Free Atoms and Particles,* Academic Press, New York, 1980.

3 (a) J. C. Negrel, R. W. Zoellner, M. Chanon and F. Chanon, in M. Chanon, M. Julliard and J. C. Poite (eds.), *Paramagnetic Organometallic Species in Activation/Selectivity Catalysis,* NATO ASI Series, Kluwer, Dordrecht, 1989, p. 109; (b) F. W. S. Benfield, M. L. H. Green, J. S. Ogden and D. Young, *J. Chem. Soc., Chem. Commun.,* (1973) 866; (c) J. C. Negrel, R. W. Zoellner and M. Chanon, *Chimia, 44* (1990) 59; (d) K. J. Klabunde, *Chemistry of Free Atoms and Particles,* Academic Press, New York, 1980, p. 89, and refs. therein.

4 B. P. Mundy and M. G. Ellerd, *Name Reactions and Reagents in Organic Synthesis,* Wiley–Interscience, New York, 1988, p. 213.

5 (a) H. Matsumoto, S. Inaba and R. D. Rieke, *J. Org. Chem., 48* (1983) 840; (b) T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc., 101* (1983) 7547; (c) M. F. Semmelhack, P. Helquist, L. D. Jones, L. Keller, L. Mendelson, L. S. Ryono, J. G. Smith and R. D. Stauffer, *J. Am. Chem. Soc., 103* (1981) 6460.

6 (a) G. W. Ebert and R. D. Rieke, *J. Org. Chem., 53* (1988) 4482; *49* (1984) 5280; (b) P. E. Fanta, *Synthesis,* (1974) 9; *Chem. Rev., 64* (1964) 613; (c) R. G. R. Bacon and H. A. O. Hill, *Q. Rev. Chem. Soc., 19* (1965) 95; (d) T. Cohen and I. Cristea, *J. Am. Chem. Soc., 98* (1976) 748; (e) T. Cohen and J. G. Tirpak, *Tetrahedron Lett.,* (1975) 143.

7 S. E. Douglass, S. T. Massey, S. G. Woolard and R. W. Zoellner, *Transition Met. Chem., 15* (1990) 317.

8 P. S. Skell and M. S. Cholod, *J. Am. Chem. Soc., 91* (1969) 6035; R. E. Mackenzie and P. L. Timms, *J. Chem. Soc., Chem. Commun.,* (1974) 650.

9 W. Wolfsberger and H. Schmidbaur, *Synth. React. Inorg. Met.-Org. Chem., 110* (1977) 2382.

10 G. W. Gokel, P. P. Widera and W. P. Weber, *Org. Synth., 55* (1976) 96.

11 P. Main, L. Lessinger, M. M. Woolfson, G. Germain and J. P. Declercq, *MULTAN 77,* a system of computer programs for the automated solution of crystal structures from X-ray diffraction data, Universities of York, UK and Louvain la Neuve, Belgium, 1977.

12 B. A. Frenz, in H. Schenk, R. Olthof-Hazelkamp, H. van Koningsveld and G. C. Bassi (eds.), *Computing in Crystallography,* Delft University Press, Netherlands, 1978, pp. 64–71.

13 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. UcKo, D. J. Barton, D. Stowens and S. J. Lippard, *Inorg. Chem., 15* (1976) 1155.

14 (a) P. L. Timms, *J. Chem. Soc., Chem. Commun.,* (1968) 1525; P. L. Timms, *J. Chem. Soc., Dalton Trans.,* (1972) 830; (b) P. L. Timms, *Angew. Chem., Int. Ed. Engl., 14* (1975) 273; K. J. Klabunde, *J. Fluorine Chem., 7* (1976) 95.

15 H. Schmidbaur, J. Adlkofer and K. Schwirten, *Chem. Ber., 105* (1972) 3382; A. G. Massey, in A. F. Trotman-Dickenson (ed.), *Comprehensive Inorganic Chemistry,* Pergamon, Oxford, 1973, p. 38.

16 (a) A. Henglein, *Current Chem., 143* (1987) 113; (b) J. Belloni, M. O. Delcourt, J. L. Marignier and J. Amblar, in P. Hedvig, L. Nyikos and R. Schiller (eds.), *Radiation Chemistry,* Akadémiai Kiadó, Budapest, 1987, p. 89.

17 J. Khatouri, *Thesis,* Orsay, France, 1992.

18 J. M. Saveant, *Adv. Phys. Org. Chem., 26* (1990) 1.

19 K. J. Klabunde, G. H. Jeong, A. W. Olsen, in J. A. Davies, P. L. Watson, A. Greenberg and J. F. Liebman (eds.), *Selective Hydrocarbon Activation: Principles and Progress,* VCH, New York, 1990, pp. 433–466.

20 M. R. A. Blomberg, P. E. M. Siegbahn and M. Svensson, *J. Am. Chem. Soc., 114* (1992) 6095.