Journal of Organometallic Chemistry, 273 (1984) 263–273
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CHEMICAL BEHAVIOUR OF THE AZIDO GROUP BONDED TO COPPER(I): SYNTHESIS AND REACTIVITY OF THIOTHIATRIAZOLATO AND ALKYNYL COMPLEXES

GIROLAMO LA MONICA, GIANATTILIO ARDIZZOIA, SERGIO CENINI
and FRANCESCA PORTA

Dipartimento di Chimica Inorganica e Metallorganica, C.N.R. Center, Via G. Venezian 21, Milano (Italy)

(Received April 9th, 1984)

Summary

The copper(I) azido-derivatives, $(PPh_3)(phen)CuN_3$ (Ia) and $(PPh_3)(TMP)CuN_3$ (Ib) (phen = 1,10-phenanthroline; TMP = 3,4,7,8-tetramethyl-1,10-phenanthroline), obtained from $[(PPh_3)_2CuN_3]_2$ and the bidentate ligand (biL), react with CS_2 to give the thiothiatriazolato-copper(I) complexes, $(PPh_3)(phen)Cu{-}N{-}C(S){-}S{-}N{=}N$ (IIa) and $(PPh_3)(TMP)Cu{-}N{-}C(S){-}S{-}N{=}N$ (IIb). The preparation of IIa and IIb occurs only when free triphenylphosphine is present in the reaction medium. The isothiocyanate complexes, $(PPh_3)(biL)Cu(NCS)$ (biL = phen, IIIa; biL = TMP, IIIb) are formed, instead of IIa and IIb, when free PPh_3 is not added to the reaction medium. The complexes IIIa and IIIb are also obtained when CH_2Cl_2 solutions of IIa and IIb are stirred for 15 h in the absence of light; if longer reaction times are used, the dimeric isothiocyanato complexes $[(biL)Cu(NCS)]_2$ are formed. Compounds IIa and IIb react with PhCOCl to give $(PPh_3)(biL)CuCl$ and 4-benzoyl-1,2,3,4-thiatriazole-5-thione, $PhCO{-}N{-}C(S){-}S{-}N{=}N$.

Treatment of Ia and Ib, or $[(PPh_3)_2CuN_3]_2$, with COS did not lead to isolation of characterizable products. An unsaturated molecule such as ethyl propriolate, $EtO_2CC{\equiv}CH$, does not behave as a 1,3-dipolarophile in its reactions with Ia and Ib, the alkynyl derivatives $[(biL)Cu_2(C{\equiv}C{-}CO_2Et)_2]_n$ (n is probably 2; biL = phen, IVa; biL = TMP, IVb), being obtained. Similarly the azido-complex $[(PPh_3)_2CuN_3]_2$ reacts with ethyl propiolate to give the asymmetric binuclear alkynyl derivative, $(PPh_3)_3Cu_2(C{\equiv}C{-}CO_2Et)_2$ (V). The reaction of V with hydrogen chloride gives $EtO_2C{-}C{\equiv}CH$ and the known complex $(PPh_3)_3Cu_2Cl_2$, confirming the above formulation. The reactions of V with neutral ligands such as TMP, phen and CyNC have also been studied, leading to the isolation of new copper(I) alkynyl-derivatives.

Introduction

Under suitable conditions, an azido group coordinated to a metal center behaves as it does in an organic azide [1]; in particular the metal–N_3 group acts as a

0022-328X/84/$03.00 © 1984 Elsevier Sequoia S.A.

TABLE 1. ANALYTICAL DATA

Compound		Colour	M.p. (°C)	Analyses (Found(calcd.)(%))		
				C	H	N
Ia	$(PPh_3)(phen)CuN_3$ [a]	Yellow	195 (dec.)	65.28 (65 75)	4.12 (4.2)	12.64 (12.8)
Ib	$(PPh_3)(TMP)CuN_3$ [b]	Yellow	200 (dec.)	67.43 (67.6)	4.98 (5.14)	11.27 (11.60)
IIa	$(PPh_3)(phen)Cu{-}\overline{N{-}C(S)S{-}N{\equiv}N}$ [c]	Yellow	80 (dec.)	59.96 (59.66)	3.84 (3.69)	10.98 (11.22)
IIb	$(PPh_3)(TMP)Cu{-}\overline{N{-}C(S){-}S{-}N{=}N}$ [d]	Yellow	80 (dec.)	61.77 (61.81)	4.68 (4.56)	9.91 (10.3)
IIIa	$(PPh_3)(phen)Cu(NCS)$	Yellow	215	66.31 (66.0)	3.93 (4.08)	7.40 (7.45)
IIIb	$(PPh_3)(TMP)Cu(NCS)$	Yellow	220	67.27 (67.8)	5.12 (5.0)	6.54 (6.78)
IVa	$[(phen)Cu_2(C{\equiv}CCO_2Et)_2]_2$ [e]	Pale-yellow	158 (dec.)	52.44 (52.70)	3.77 (3.59)	5.39 (5.59)
IVb	$[(TMP)Cu_2(C{\equiv}CCO_2Et)_2]_2$	White	160 (dec.)	55.81 (56.0)	4.78 (4.67)	5.03 (5.03)
V	$(PPh_3)_3Cu_2(C{\equiv}CCO_2Et)_2$ [f]	White	155	69.44 (69.38)	5.18 (4.97)	– –
VI	$[(PPh_3)(CyNC)Cu(C{\equiv}CCO_2Et)]_2$ [g]	White	144	68.15 (67.73)	5.81 (5.83)	2.65 (2.64)
VIIa	$(PPh_3)(phen)Cu(C{\equiv}CCO_2Et)$ [h]	Yellow	150 (dec.)	69.11 (69.71)	4.67 (4.65)	4.82 (4.65)
VIIb	$(PPh_3)(TMP)Cu(C{\equiv}CCO_2Et)$	Yellow	160 (dec.)	71.36 (71.07)	5.52 (5.47)	4.38 (4.25)
VIII	$[(TMP)Cu(C{\equiv}CCO_2Et)]_4 \cdot H_2O$ [i]	Salmon- -pink	165 (dec.)	62.48 (62.84)	5.42 (5.36)	7.09 (6 98)
IX	$(TMP)(CyNC)Cu(C{\equiv}CCO_2Et)$	Pale-yellow	130	65.84 (66.47)	6 33 (6.33)	8.48 (8.31)

[a] phen = 1,10-phenanthroline. [b] TMP = 3,4,7,8-tetramethyl-1,10-phenanthroline. [c] S, 10.04 (10 26); mol. wt., 570 (CH_2Cl_2) (623.5). [d] S, 9 35 (9.42); mol. wt., 623 (CH_2Cl_2) (679.5). [e] O, 13.4 (12.77). [f] O, 5.78 (5.78), mol. wt., 843 (CH_2Cl_2) (1107) (the values found are dependent on concentration) [g] Mol. wt , 497 (CH_2Cl_2) (531.5). [h] Mol. wt., 523 (CH_2Cl_2) (602.5) (the values found are dependent on concentration). [i] O, 8.45 (8 97), Cu, 15.82 (15 83) For complex VIII, repeated molecular weight measurements in CH_2Cl_2 always gave values of ca 450.

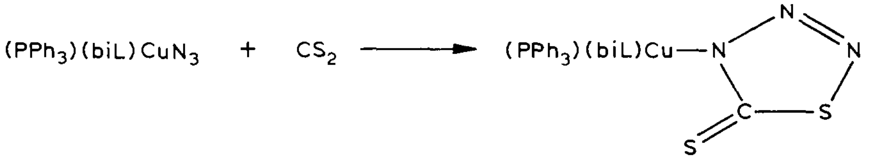
1,3-dipolar reagent towards dipolarophiles such as carbon disulphide and alkynes [2–5]. These reactions sometimes give a five-membered heterocycle which is bonded to the metal atom.

In this paper we report the reactions of CS_2 and of the activated terminal alkyne $EtO_2C{-}C{\equiv}CH$ with known and new azido complexes of copper(I), which give thiothiatriazolato derivatives and alkynyl complexes, respectively.

Results and discussion

I. Synthesis and reactions of the thiothiatriazolato complexes II

The addition of CS_2 to a benzene suspension of the new azido complexes of copper(I), $(PPh_3)(phen)CuN_3$ (Ia) and $(PPh_3)(TMP)CuN_3$ (Ib), obtained from $[(PPh_3)_2CuN_3]_2$ and the bidentate ligand, leads to the formation of thiothiatriazolato-derivatives of copper(I) according to eq. 1:



(1)

(II)

(IIa, biL = 1,10-phenanthroline ;
IIb, biL = 3,4,7,8-tetramethyl-1,10-phenanthroline)

The yellow triazolato complexes II are insoluble in the reaction medium. Free triphenylphosphine and the absence of light are normally necessary for compounds II to be obtained (see later). For these derivatives to be prepared in the absence of free phosphine, concentrated solutions must be used.

The formula shown for complexes II is based on elemental analyses and molecular weight determinations (Table 1). The IR spectra (Table 2) show the disappearance of the asymmetric azide stretching band (2030–2040 cm^{-1}) and the appearance of the characteristic IR bands of the five-membered heterocyclic anion which would be formed by the 1,3-dipolar cycloaddition of the azide moiety to the dipolarophile CS_2 [2]. The most characteristic IR band for the thiothiatriazolato complexes described here appears at ca. 1200 cm^{-1}: this absorption can be attributed to the thiocarbonyl group [2] and lies about 100 cm^{-1} lower in energy than the one observed for organo-substituted thiothiatriazoles [6a].

The complexes II show a moderate tendency to decompose, both in the solid state and in solution, on gentle heating or through the action of light. On the other hand no decomposition was apparent when they are kept in the dark at 0 °C.

Decomposition of the thiothiatriazolato derivatives

When a CH_2Cl_2 solution of IIa is refluxed in the dark for 7 h, an orange product is precipitated. The IR spectrum of this product is identical to that of $[(phen)Cu(NCS)]_2$ prepared by reacting $[Cu(NCS)]_n$ with 1,10-phenanthroline. The presence of triphenylphosphine sulfide in the mother liquor was confirmed. It thus

TABLE 2

INFRARED DATA (Nujol (cm^{-1}))

Compound	Significant absorptions
Ia	2040 $\nu_{as}(N_3)$
Ib	2030 $\nu_{as}(N_3)$
IIa	1195 ν(C=S)
IIb	1210 ν(C=S)
IIIa	2090 ν(NCS)
IIIb	2095 ν(NCS)
$EtO_2CC{\equiv}CH$	2120 $\nu(C{\equiv}C)^a$; 1715 $\nu(C{=}O)^a$
IVa	2100, 1935 $\nu(C{\equiv}C)$; 1685 $\nu(C{=}O)^b$
IVb	2090, 1920 $\nu(C{\equiv}C)$; 1675 $\nu(C{=}O)$
V	2050 $\nu(C{\equiv}C)$; 1690 $\nu(C{=}O)^b$
VI	2170 ν(NC); 2035 $\nu(C{\equiv}C)$; 1670 $\nu(C{=}O)$
VIIa	2050 $\nu(C{\equiv}C)$; 1660 $\nu(C{=}O)^b$
VIIb	2045 $\nu(C{\equiv}C)$; 1665 $\nu(C{=}O)$
VIII	2060 $\nu(C{\equiv}C)$; 1660 $\nu(C{=}O)$
IX	2145 ν(NC); 2055 $\nu(C{\equiv}C)$; 1670 $\nu(C{=}O)$

[a] CH_2Cl_2 solution. [b] The absorption assigned to $\nu(C{=}O)$ appears as a close doublet.

appears that the thermal decomposition of IIa proceeds according to eq. 2:

$$\underset{(IIa)}{2(PPh_3)(phen)Cu{-}\overline{N{-}C(S){-}S{-}N{=}N}} \rightarrow [(phen)Cu(NCS)]_2 + 2\ Ph_3PS + 2\ N_2 \qquad (2)$$

We have found that if the reagents shown in eq. 1 are mixed in the dark in dilute benzene solution and in the absence of free PPh_3, isothiocyanato derivatives of formula $(PPh_3)(biL)Cu(NCS)$ (III) are formed instead of the thiothiatriazolato complexes II, (eq. 3):

$$\underset{(I)}{(PPh_3)(biL)CuN_3} + CS_2 \rightarrow \underset{(III)}{(PPh_3)(biL)Cu(NCS)} + S + N_2 \qquad (3)$$

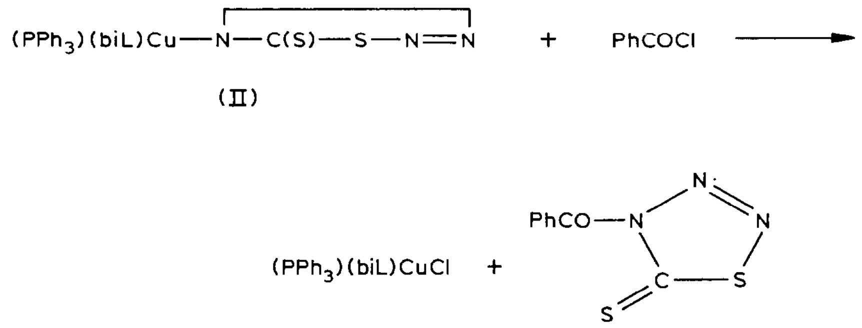
(IIIa, biL = 1,10-phenanthroline;

IIIb, biL = 3,4,7,8-tetramethyl-1,10-phenanthroline)

The same isothiocyanato complexes have been isolated when CH_2Cl_2 solutions of the thiothiatriazolato complexes II were stirred for 15 h at room temperature in the absence of light. When longer times are used, these intermediate complexes III are converted into the insoluble derivatives $[(biL)Cu(NCS)]_2$. On the basis of these results, it seems clear that the triazolato complexes II can be isolated only if the dissociation of the phosphine ligand is prevented. This is further indicated by the fact that complexes II are similarly obtained, even in the absence of free PPh_3, when concentrated solutions are used.

Cleavage of the coordinated triazole

When PhCOCl is added in the dark to a benzene suspension of the triazolato complexes II at room temperature over 3 h, the following reaction takes place:



(4)

The formation of these chloro–copper(I) complexes, which are insoluble in the reaction medium, was confirmed by elemental analyses and by their IR spectra, which are identical to those of authentic samples.

The presence in the mother liquor of 4-benzoyl-1,2,3,4-thiatriazole-5-thione was confirmed by its IR and mass spectra, which are identical with those of an authentic sample prepared according to the literature [6a,6b].

When methyl iodide was reacted with IIb using the same conditions as with PhCOCl, $(PPh_3)(TMP)CuI$ (TMP = 3,4,7,8-tetramethyl-1,10-phenanthroline) was obtained as the insoluble product. The mother liquor gave an oily loathsome residue which showed in its IR spectrum the characteristic absorptions of the five-membered heterocyclic thiatriazole with a significant $\nu(C{=}S)$ band at ca. 1300 cm^{-1} [6a].

Reaction of $[(PPh_3)_2CuN_3]_2$ with COS

Azidobis(triphenylphosphine)copper(I) was reacted with COS to see which of the possible modes of 1,3-dipolar cycloaddition to the azido group takes place. This reaction was carried out in a CH_2Cl_2 solution at 0 °C using a COS atmosphere. After a few minutes the absorption due to the $\nu_{as}(N_3)$ of the starting azido complex disappeared from the IR spectrum, while a new band at 2140 cm^{-1} was present. Attempts to isolate an analytically pure complex were unsuccessful. The disappearance of the $\nu(N_3)$ during the reaction can be explained by the possible intermediate formation of a triazolato–copper(I) derivative, which in this case is highly unstable. In fact we assume that the new absorption at 2140 cm^{-1} is to be attributed to a decomposition product of the intermediate triazolato complex. On the basis of the assignments suggested by Norbury [7], we exclude the possibility that the absorption observed at 2140 cm^{-1} could be due to terminal NCS or NCO groups in the non-isolable decomposition product. Among the other possibilities (bridging NCO or NCS and terminal SCN) we suggest tentatively that a terminal *S*-bonded thiocyanate is present in this non-isolable complex, which is probably formed via the 1,3-dipolar cycloaddition intermediate, $(PPh_3)_nCu{-}\overline{N{-}C(S){-}O{-}N{=}N}$ [3,4].

From the CH_2Cl_2 solution on standing, a brown material precipitated, which was insoluble in common organic solvents. Its IR spectrum did not show any significant band other than those due to triphenylphosphine. Qualitative analysis confirmed the presence in this material of sulfur and it is probably a polymeric derivative in which the sulfur is bonded to copper atoms. The nature of this product was not further investigated.

The analogous reactions of COS with Ia and Ib did not lead to the isolation of characterizable products.

II. Synthesis of alkynyl complexes of copper(I)

The terminal alkyne $EtO_2CC{\equiv}CH$ reacts with the copper(I) azido derivatives Ia and Ib as indicated in eq. 5:

$$\underset{(I)}{(PPh_3)(biL)CuN_3} \xrightarrow{EtO_2CC\equiv CH} \underset{(IV)}{[(biL)Cu_2(C{\equiv}CCO_2Et)_2]_n} \tag{5}$$

(IVa, biL = phen; IVb, biL = TMP)

The reactions were carried out in the alkyne as solvent, IVa and IVb being obtained as white insoluble products. The formula showing complexes IV as copper(I) alkynyl derivatives is based on repeated elemental analyses, including oxygen analysis, and on their IR spectra. No molecular weight measurements were obtained because of the low solubility in common organic solvents. We tentatively assign tetrameric structures to these products (see later).

The IR spectra of IVa and IVb are worthy of mention. In the 1900–2100 cm^{-1} region, two significant strong absorptions are present. Both of these bands are due to the $\nu(C{\equiv}C)$ of the alkynyl ligands. We assign the higher band to the $\nu(C{\equiv}C)$ of an alkynyl group not involved in the coordination with another copper atom. This band lies at a frequency only 20–30 cm^{-1} lower than that of free ethyl propiolate. A similar effect has been observed in octahedral cobalt(III) alkynyl complexes [5]. The second absorption, whose frequency is ca. 200 cm^{-1} lower than $\nu(C{\equiv}C)$ for free ethyl propiolate, can be assigned to a $C{\equiv}C$ bond having a rather strong interaction with the metal centers.

A related tetrameric alkynyl complex of copper(I), $[(Me_3P)Cu(C{\equiv}CPh)]_4$ has been reported [8] and its crystal structure determined [9]. Two $\nu(C{\equiv}C)$ bands were also observed in this case, but they appeared as very close together (2019 and 2045 cm^{-1}), suggesting that the $C{\equiv}C$ bonds of the four phenylethynyl substituents are quite similar in their involvement in the coordination. The phosphine complex has the four phosphine ligands bound to only two copper atoms. In our case the two bidentate ligands could be analogously involved in the coordination with only two copper atoms.

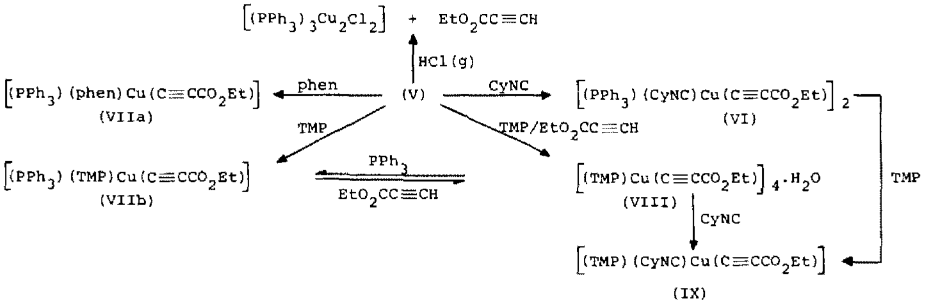
A binuclear alkynyl derivative has been obtained by reacting the known azidobis(triphenylphosphine)copper(I), $[(PPh_3)_2CuN_3]_2$, with ethyl propiolate, eq. 6:

$$[(PPh_3)_2CuN_3]_2 \xrightarrow{EtO_2CC\equiv CH} \underset{(V)}{(PPh_3)_3Cu_2(C{\equiv}CCO_2Et)_2} \tag{6}$$

The reaction was carried out at room temperature in a benzene-ethanol mixture. During the formation of V, which is insoluble in the reaction mixture, gas evolution was observed. It is known [5] that terminal alkynes can act as CH acids, undergoing a ligand substitution reaction, or as dipolarophiles, giving 1,3-dipolar cycloadditions. The formation of the alkynyl complex V indicates that the ethyl propriolate behaves as a CH acid toward the azido complex $[(PPh_3)_2CuN_3]_2$.

Alkynyl-phosphine complexes of copper(I) have been reported [8]. They are usually prepared by the addition of the tertiary phosphine to a suspension of the insoluble ethynyl compound, $[Cu(C{\equiv}C{-}R)]_n$, in an organic solvent. Recently alkynyl-phosphine copper(I) derivatives have been obtained by reacting 1-alkynes with pentamethylcyclopentadienyl-phosphine complexes of copper(I) [10].

The formula of complex V is supported by elemental analyses, molecular weight measurements at different concentrations, and by its reactivity (see later). Its IR spectrum shows a significant strong band at 2050 cm^{-1}, assignable to the $\nu(C\equiv C)$ of the alkynyl group. This absorption lies at a frequency 70 cm^{-1} lower than that of the free alkyne, suggesting a weak π-interaction of the triple bond of the alkynyl substituent bound to a copper atom, with the second metal center. Thus the alkynyl complex V reported here seems to be a new member of the copper(I) derivatives of general formula $L_3Cu_2X_2$. Complexes of this type (X = halogen) have been reported, and the crystal structure determined in the case where L = PPh_3 and X = Cl, confirming the unusual stoichiometry [11]. The formula of complex V has been confirmed by reacting it in benzene with hydrogen chloride (see Scheme 1), when ethyl propiolate and the known dichlorotris(triphenylphosphine)dicopper(I) were the only products.



SCHEME 1

The dimeric nature of V was unchanged in its reaction with cyclohexyl isocyanide. From this reaction (see Scheme 1) a product which analysed as $[(PPh_3)(CyNC)Cu(C\equiv CCO_2Et)]_2$ (VI) has been obtained. Its IR spectrum is in agreement with this formula, two significant bands being present in the 2000–2200 cm^{-1} region (see Table 2). In this case the coordinated cyclohexyl isocyanide acts as a pure σ-donor ligand. The alkynyl complex V reacts with the bidentate ligand 1,10-phenanthroline yielding (VIIa) (see Scheme 1). Analytical data, IR spectrum and molecular weight measurements confirmed the nature of VIIa as a tetracoordinated copper(I) alkynyl derivative. Surprisingly, the $\nu(C\equiv C)$ of VIIa (2050 cm^{-1}) (Table 2) lies at the same frequency as for V, although in this case no π-interaction involving the $C\equiv C$ bond is expected.

The related tetramethyl-1,10-phenanthroline complex VIIb, has been obtained analogously by using cyclohexane as the reaction medium. When VIIb, suspended in benzene, was stirred in the presence of free ethyl propiolate a slow solubilization was observed. After ca. 0.5 h a yellow product, (VIII), precipitated (see Scheme 1). It was recovered by filtration and washed with diethyl ether, yielding a salmon-pink compound. Repeated oxygen analyses indicated the presence of more oxygen than that required on the basis of the formula $[(TMP)Cu(C\equiv CCO_2Et)]_n$. Thermogravimetric analysis has shown unambiguously that water is present in the complex VIII, with a Cu:H_2O ratio of 4. The role of the added alkyne, in giving VIII from VIIb, is to remove the phosphine ligand from the metal by forming an adduct with it. The same adduct, whose identity is not yet known, has been obtained by reacting free triphenylphosphine with ethyl propiolate. VIII can also be prepared in high yields, in a one step reaction, by treating V with TMP in the presence of the propiolate ester for 7 h in wet benzene. Compound VIII can readily be converted into VIIb by reacting it in benzene with PPh_3 at room temperature (Scheme 1). Another addition product was obtained from VIII by reacting it with cyclohexyl isocyanide, the complex $(TMP)(CyNC)Cu(C{\equiv}CCO_2Et)$ (IX) being isolated. Its IR spectrum showed two significant strong bands at 2055 and 2145 cm^{-1} attributable to $\nu(C{\equiv}C)$ and $\nu(NC)$, respectively, the latter being practically unchanged relative to that of the free cyclohexyl isocyanide.

Complex VIIa, $(PPh_3)(phen)Cu(C{\equiv}CCO_2Et)$, did not react with the free alkyne to give the derivative analogous to VIII, even when the reaction was carried out at 50 °C.

Among the copper(I) alkynyl complexes reported in the present work, compound VIII appears to be the most reactive species. Preliminary results have shown that it reacts readily with interesting molecules such as H_2, O_2 and CO_2, and the products of such reactions are at the moment under investigation.

Experimental

The complex $[(PPh_3)_2CuN_3]_2$ was obtained by a metathetical reaction from $(PPh_3)_3CuCl$ and NaN_3 in CH_2Cl_2. Oxygen analyses and molecular weight determinations were performed by Pascher Laboratory (Bonn). IR spectra were recorded on a Beckman 4210 instrument. All the reactions were carried out under a nitrogen atmosphere.

Preparation of $(PPh_3)(phen)CuN_3$ (Ia) and $(PPh_3)(TMP)CuN_3$ (Ib) (phen = 1,10-phenanthroline; TMP = 3,4,7,8-tetramethyl-1,10-phenanthroline)

To a CH_2Cl_2 solution containing the bidentate ligand, biL, $[(PPh_3)_2CuN_3]_2$ was added with stirring (biL:Cu ratio = 1.1). The resulting solution rapidly became orange. After 1 h it was evaporated to dryness and the residue treated several times with toluene. The yellow complexes Ia and Ib were filtered off, washed with n-hexane and dried in vacuo.

Reactions of Ia and Ib with CS_2

To a benzene solution (15 ml) containing PPh_3 (0.38 mmol) and freshly distilled CS_2 (3.3 mmol), Ia or Ib (0.3 mmol) was added. The yellow suspension was stirred in the dark until the IR spectrum of the insoluble yellow compound did not show the $\nu_{as}(N_3)$ of the starting azido complexes (ca. 6 h). The thiothiatriazolato complexes IIa or IIb were recovered by filtration, washed with benzene, n-hexane and dried in vacuo. They can be stored in the dark at 0 °C for weeks with no apparent decomposition.

Decomposition of IIa

(a) A CH_2Cl_2 solution of IIa was refluxed in the dark for ca. 6 h. The insoluble orange product was filtered off, washed with CH_2Cl_2 and dried in vacuo. Analytical data supported its formulation as $[(phen)Cu(NCS)]_2$. Its IR spectrum ($\nu(NCS)$ 2110 cm^{-1}) was identical to that of an authentic sample prepared from $[Cu(NCS)]_n$ and 1,10-phenanthroline in methanol suspension for 12 h. In the mother liquor of the thermal decomposition reaction, the presence of triphenylphosphine sulfide was confirmed.

(b) A CH_2Cl_2 solution of IIa was stirred in the dark at room temperature for 15 h. An IR spectrum of the solution showed the presence of a strong absorption at 2085 cm^{-1}. The solution was evaporated to dryness and the residue treated with diethyl ether, filtered off and dried in vacuo. Its IR spectrum was identical to that of an authentic sample of $(PPh_3)(phen)Cu(NCS)$, IIIa, prepared from $[Cu(NCS)]_n$, 1,10-phenanthroline and PPh_3 in methanol (ν(NCS) 2095 cm^{-1}).

If the CH_2Cl_2 solution of IIa is stirred for longer times (ca. 30 h), an orange precipitate is formed. This was confirmed to be $[(phen)Cu(NCS)]_2$, described in (a). The complexes IIIa and $(PPh_3)(TMP)Cu(NCS)$, IIIb, are the final products of the reaction of Ia or Ib with CS_2 if free triphenylphosphine is not present in the reaction medium (see text).

Cleavage of IIa or IIb with PhCOCl and MeI

To a benzene suspension (10 ml) of IIa or IIb (0.05 g), freshly distilled benzoyl chloride (0.2 ml) is added with stirring at room remperature under moisture-free conditions and in the dark. After 3 h the insoluble yellow product was filtered off. It was confirmed as $(PPh_3)(phen)CuCl$ or $(PPh_3)(TMP)CuCl$ by elemental analyses and by comparing its IR spectrum with that of an authentic sample prepared by reacting $(PPh_3)_3CuCl$ with either phen or TMP in diethyl ether.

The mother liquor of the cleavage reaction was evaporated to dryness, to produce a pale yellow oily residue. This was treated with diethyl ether and filtered from further amounts of the above copper(I) chloro-complex. The ether solution was evaporated to dryness and n-hexane was added. The insoluble white product was shown to be 4-benzoyl-1,2,3,4-thiatriazole-5-thione by elemental analysis and by comparing its IR and mass spectra with those of an authentic sample prepared according to the literature method [6b].

The reaction of IIb with methyl iodide was similarly carried out. The benzene-insoluble crystalline yellow product was shown to be $(PPh_3)(TMP)CuI$ by its elemental analysis. From the mother liquor an oily residue was obtained. Attempts to obtain an analytically pure product were useless. Nevertheless the IR spectrum of this material showed bands which can be associated with the presence of 4-methyl-1,2,3,4-thiatriazole-5-thione [6a].

Synthesis of $[(phen)Cu_2(C{\equiv}CCO_2Et)_2]_2$ *(IVa) and* $[(TMP)Cu_2(C{\equiv}CCO_2Et)_2]_2$ *(IVb)*

Ethyl propiolate (0.5 ml) was added with stirring to Ia or Ib (0.05 g). A clear solution was obtained within 15 min, from which IVa or IVb formed as insoluble products. They were filtered off, washed with benzene and n-hexane and dried in vacuo.

Synthesis of $(PPh_3)_3Cu_2(C{\equiv}CCO_2Et)_2$ *(V)*

To an ethanol-benzene mixture (10 ml, 5 : 1) containing ethyl propiolate (0.2 ml), $[(PPh_3)_2CuN_3]_2$ (0.25 g) was added with stirring. After 1 h a yellow solution formed, while gas evolution occurred. After ca. 5 h the insoluble white product was filtered off, washed with the ethanol-benzene mixture and dried in vacuo. In the mother liquor the presence of free triphenylphosphine was confirmed.

Reaction of V with HCl(g)

Gaseous HCl was bubbled for 5 min through benzene (10 ml), and V (0.05 g) was added with stirring. A clear solution formed. After 15 min it was evaporated to dryness and the residue treated with diethyl ether. The insoluble white product gave an elemental analysis in agreement with its formulation as $(PPh_3)_3Cu_2Cl_2$. In the filtered diethyl ether the presence of ethyl propiolate as the only product was confirmed by IR spectroscopy.

Reaction of V with cyclohexyl isocyanide

To a benzene solution (6 ml) containing CyNC (0.1 ml), V (0.1 g) was added with stirring. A clear solution rapidly formed. After 3 h it was evaporated to dryness and the residue treated with n-hexane and then with diethyl ether. The insoluble white product VI, was filtered off, washed with diethyl ether and dried in vacuo.

Reaction of V with phen or TMP

To a benzene suspension (10 ml) of V (0.09 g), 1,10-phenanthroline (0.04 g) was added with stirring. The yellow insoluble product VIIa rapidly formed. After 3 h it was filtered off, washed with a little benzene and n-hexane and dried in vacuo.

The same complex, VIIa, can be obtained by using CH_2Cl_2 as the reaction medium. The yellow solution obtained is evaporated to dryness and toluene is added, giving VIIa as the insoluble product.

To a cyclohexane suspension (20 ml) of V (0.1 g), 3,4,7,8-tetramethyl-1,10-phenanthroline (0.055 g) was added with stirring. After 12 h the yellow insoluble complex VIIb was filtered off. It was stirred for 2 h as a benzene suspension, to remove the excess TMP, and then recovered by filtration.

Reaction of V with TMP in the presence of $EtO_2CC{\equiv}CH$

To a benzene solution (8 ml) of ethyl propiolate (0.3 ml), 3,4,7,8-tetramethyl-1,10-phenanthroline (0.051 g) and the alkynyl complex V (0.1 g) were added with stirring. After 12 h a yellow insoluble product formed. It was filtered off and washed with diethyl ether to give the complex VIII as a salmon-pink derivative. The reaction is faster if wet benzene is used. The alkynyl complex VIII can also be prepared by stirring for 20 h the complex VIIb, obtained as described above, with ethyl propiolate in benzene.

Reaction of VIII with PPh_3 or CyNC

To a benzene solution (8 ml) of PPh_3 (0.18 g), complex VIII (0.1 g) is added with stirring. After 15 min, a yellow solution formed. From this an insoluble yellow product precipitated. After 2 h it was filtered off, washed with benzene and n-hexane and dried in vacuo. Its elemental analysis and IR spectrum were in agreement with a formulation as complex VIIb.

To a benzene solution (6 ml) containing CyNC (0.1 ml), VIII (0.05 g) was added with stirring. A yellow-orange solution formed. After 2 h it was evaporated to dryness and the residue treated with n-hexane and diethyl ether. The yellow complex, IX, was filtered off, washed with diethyl ether and dried in vacuo. The complex IX can also be obtained by reacting VI with TMP in benzene.

Acknowledgement

We thank Dr. L. Erre (Università di Sassari) for thermogravimetric determinations.

References

1 Z. Dori and R.F. Ziolo, Chem. Rev., 73 (1973) 247, and refs. therein.

2 (a) R.F. Ziolo and Z. Dori, J. Am. Chem. Soc., 90 (1968) 6560; (b) R.F. Ziolo, J.A. Thich and Z. Dori, Inorg. Chem., 11 (1972) 626.

3 L. Busetto, A. Palazzi and R. Ros, Inorg. Chim. Acta, 13 (1975) 233.

4 W. Rigby, P.M. Bailey, J.A. McCleverty and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1979) 371.

5 T. Kemmerich, J.H. Nelson, N.E. Takach, H. Boehme, B. Jablanski and W. Beck, Inorg. Chem., 21 (1982) 1226.

6 (a) E. Lieber, C.N. Pillai, J. Ramachandran and R.D. Hites, J. Org. Chem., 22 (1957) 1750; (b) L.F. Audrieth, J.R. Johnson and A.W. Browne, J. Am. Chem. Soc., 52 (1930) 1928.

7 A.H. Norbury, Adv. Inorg. Chem. Radiochem., 17 (1975) 231.

8 G.E. Coates and C. Parkin, J. Inorg. Nucl. Chem., 22 (1961) 59.

9 P.W.R. Corfield and H.M.M. Shearer, Acta, Crystallogr., 21 (1966) 957.

10 H. Werner, H. Otto, T. Ngo-Khac and Ch. Burschka, J. Organomet. Chem., 262 (1984) 123.

11 D.F. Lewis, S.J. Lippard and P.S. Welcker, J. Am. Chem. Soc., 92 (1970) 3805, and refs. therein.