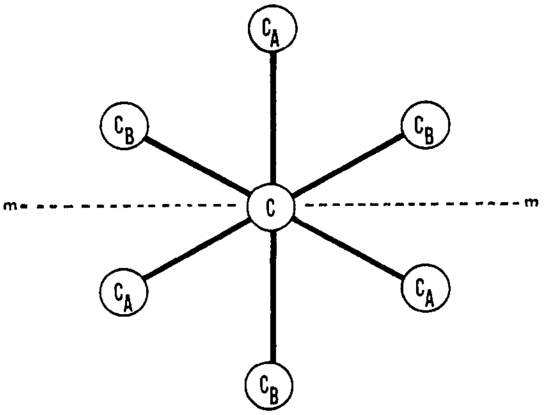

Figure 4.—View down the -C–N–C axis of the isocyanide ligands showing the disorder of the methyl groups. Atoms labeled C_A and C_B belong to the distinct conformations of the disordered *tert*-butyl group. For those ligands that lie on the crystallographic mirror plane (*m*– – – –*m*), the atoms C_A and C_B are related by virtue of that plane.

MoL_5X_2 (L = isocyanide; X = Cl, Br) compounds prepared by an entirely different route.[11] Seven-coordination has long been postulated[25–29] for Mo(II) complexes containing good π-acceptor ligands, notably carbonyls, and the present study provides direct confirmation of this suggestion by X-ray diffraction.[30–32] Recently cations of general formula $[Mo(CO)_2(D)_2I]^+$ (D = *o*-phen, bipy)[33] and the complex $Mo(CO)_3(dtc)_2$[34] have been reported. The resemblance between the stoichiometries of these MX_4Y_2Z and MX_4Y_3 type of molecules and that of the $[Mo(CNR)_6I]^+$ ion may be noted. Finally, we wish to emphasize that, although the C_{2v} capped trigonal prism has been identified in the solid state for iodohexakis(*tert*-butyl isocyanide)molybdenum(II) iodide, the structure of this compound in solution is as yet unknown. Because of the close energetic similarities between coordination polyhedra for the higher coordination numbers, rearrangement to one of the other structures (Table IV) or stereochemical nonrigidity[35] is entirely possible. Thus, for example, the related heptacyanomolybdate(III) ion is known from its spectroscopic properties to have a seven-coordinate pentagonal-bipyramidal structure in solution, while in the solid potassium dihydrate salt, a capped trigonal-prismatic structure has been proposed.[36] Studies of the solution structure of $[Mo(CNR)_6I]^+$ salts are currently in progress.

Acknowledgments.—We are most grateful to Miss Sandra Hoffer for her initial efforts on this problem, to Mr. Donald Barton for help with computations, to Professor Harry Gray and Dr. George Rossman for informing us of their results on the heptacyanomolybdate(III) ion prior to publication, and to the National Science Foundation for financial support. S. J. L. also thanks the Alfred P. Sloan Foundation for a research fellowship (1968–1970).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TEMPLE UNIVERSITY OF THE COMMONWEALTH SYSTEM OF HIGHER EDUCATION, PHILADELPHIA, PENNSYLVANIA 19122

Some Chemistry of Azido Complexes of Group Ib Metals

BY RONALD F. ZIOLO, JOHN A. THICH, AND ZVI DORI*

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The preparation and characterization of several azido and thiocyanato complexes of group Ib metals of the general formula ML_nX (n = 1, M = Au(I); n = 2, M = Cu(I), Ag(I); L = $P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$, $P(o\text{-}CH_3C_6H_4)(C_6H_5)_2$, $P(CH_3O)(C_6H_5)_2$, $P(C_2H_5O)(C_6H_5)_2$; $X^- = N_3^-, NCS^-$), ML′X, and $M_2L'_3X_2$ ($L' = (C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$) are reported. The azido complexes react with dipolarophiles such as CS_2 and CF_3CN by 1,3-dipolar cycloaddition to form thiothiatriazolato and perfluoromethyltetrazolato complexes. The CF_3CN adducts are stable while the CS_2 adducts decompose both thermally and photolytically. The thermal decomposition of a solution containing azidobis(triphenylphosphine)copper(I) and CS_2 in a 1:1 ratio yields triphenylphosphine sulfide, CuNCS, and thiocyanatobis(triphenylphosphine)copper(I), while the photolytic decomposition of the above solution leads to the corresponding thiocyanato complex and colloidal sulfur. The same results are observed for the other CS_2 adducts reported here. Thermal or photolytic decomposition of the complex thiothiatriazolato(triphenylphosphine)copper(I) ($Cu(P(C_6H_5)_3)N_3\cdot CS_2$) in $CHCl_3$ leads to CuNCS and triphenylphosphine sulfide. The azido complexes of Cu(I) and Ag(I) are all photolytically active and their photolysis in chloroform leads to the liberation of N_2, to the abstraction of chlorine atoms from the solvent, and to the formation of complexes such as $[Ag(P(C_6H_5)_3Cl]_4$ and $Cu_2(P(C_6H_5)_3)_3Cl_2$. The geometry of these group Ib metal complexes is discussed in terms of recent X-ray structural results and physical data obtained in solution.

Introduction

The chemistry of coordinated azides has received increased attention during the past several years primarily due to the fact that coordinated azides can be both oxidized and reduced. For example, it was shown that coordinated azides react with metal hydrides to produce amino complexes[1] or with oxygen to produce coordi-

(1) W. Beck and M. Bauder, *Chem. Ber.*, **103**, 583 (1970).

nated nitrites.[2] Another interesting reaction involves the formation of N_2-containing complexes from the corresponding azido complexes.[3] The relatively weak N–N bond of the azide moiety (the bond between the middle nitrogen and the nitrogen coordinated to the metal) leads to the conversion of N_3^- to NCO^- [4] by reaction with CO and to coordinated triphenylphosphoimido group[5] by reaction with triphenylphosphine.

The anticipation that under certain conditions coordinated azides would behave in an analogous way to organic azides has led to the preparation of coordinated five-membered heterocyclic rings such as thiothiatriazole and perfluoromethyltetrazole which result from the 1,3-dipolar addition of the dipolarophiles carbon disulfide and trifluoroacetonitrile to the azide moiety.[6,7] In this paper we report some of these reactions with azido complexes of group Ib metals.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 225 infrared spectrophotometer using Nujol mulls or KBr pressed pellets. The ultraviolet absorption spectra were recorded on a Cary 14 spectrophotometer using matched quartz cells of 1-cm path length and spectrograde solvents. Molecular weights were determined by vapor pressure osmometry (Mechrolab Model 301A) in benzene and chloroform solutions, and tga data were recorded on a Du Pont 950 thermal analyzer. Conductivity measurements were made using an Industrial Instruments bridge, Model RC16B2, and ^{19}F spectra were recorded on a Varian HA-100 spectrometer equipped with the appropriate probe.

Photolysis reactions were carried out in internally cooled Pyrex vessels containing a Hanovia Type-L 450-W medium pressure mercury vapor immersion lamp with a Vycor 7910 filter. All photolysis reactions were carried out at approximately 10° (except where noted otherwise) under Ar using dried, deaerated, reagent-grade solvents. A Hanovia "Utility" ultraviolet quartz lamp was used when irradiations were carried out on samples in Vycor vessels connected directly to a high-vacuum line. To measure the amount of nitrogen produced in the various photochemical reactions, a $CHCl_3$ solution containing the desired complex was injected into the tube and dissolved gases were removed by evacuation and freeze–thaw cycles. In the last cycle the tube was closed to the system and its contents warmed to 300°K. Irradiation was carried out for several hours. After irradiation, the mixture was again taken through several freeze–thaw cycles and the gaseous products were collected with the use of a Toepler pump into a precalibrated volume. Pressure and temperature measurements were made, and the amount of gas formed was calculated using the ideal gas equation.[8] A small sample of the gas was removed for mass spectral analysis.

Elemental analyses were performed by Micro-Analysis Inc., Wilmington, Del. 19808, and by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921. Mass spectral analysis were performed by the Morgan Schaffer Corp., Montreal, Quebec, Canada.

Reagent grade chemicals were used in the preparation of the complexes. The phosphine ligands were prepared by published methods.

I. Preparation of Azido and Thiocyanato Complexes. a. Type $M(L)_2N_3$ and $M(L)_2NCS$ ($L = P(C_6H_5)_3$, $P(CH_3)(C_6H_5)_2$, $P(o\text{-}CH_3C_6H_4)(C_6H_5)_2$; M = Cu(I), Ag(I)).—A methanolic solution of NaN_3 or NaNCS (0.02 mol) was added slowly to a warm chloroform solution containing 0.015 mol of $M(L)_3Cl$.[9] The mixture was stirred for 1 hr at room temperature. Addition of hexane caused the precipitation of the desired complex. Analytically pure samples of these complexes were obtained by recrystallization from a chloroform–hexane solution.

b. **Type $Cu(L)_2N_3$ and $Cu(L)_2NCS$ ($L = P(CH_3O)(C_6H_5)_2$, $P(C_2H_5O)(C_6H_5)_2$.**—L (0.04 mol) was added dropwise to a hot methanolic solution containing 0.015 mol of $Cu(BF_4)_2$. The resulting clear solution was stirred for 1 hr and then filtered. NaN_3 or NaNCS (0.018 mol) in methanol was then added and the solution was stirred for an additional hour. The solvent was then evaporated to a volume of 30 ml and the residue filtered. To the resulting solution, 150 ml of petroleum ether (bp 40–60°) was added. Colorless crystalline material separated out after being kept at 0° for several days. These complexes were recrystallized from a chloroform–petroleum ether (bp 40–60°) solution.

c. **$Au(P(C_6H_5)_3)X$ ($X = N_3$, NCS).**—These complexes were prepared by shaking $Au(P(C_6H_5)_3)Br$ in $CHCl_3$ with an excess of NaN_3 or NaNCS in water until the chloroform layer showed the absence of bromide.

d. **$Ag_2(diphos)_3(N_3)_2\cdot 2DMF$.**—AgCl (10 mmol) was added together with 15 mmol of diphos to 300 ml of dimethylformamide. After stirring on the steam bath for several hours the solution was filtered and 15 mmol of NaN_3 in 150 ml of hot methanol was added. The resulting solution was stirred for 1 hr. The solution was evaporated to a volume of 50 ml and filtered. The desired complex separated upon standing. Analytically pure sample was obtained by recrystallization from dimethylformamide.

Preparation of the 5-Thio-1,2,3,4-thiatriazolato Complexes.—To a stirred chloroform solution containing 0.02 mol of the azido complexes, 0.021 mol of CS_2 in 5 ml of chloroform was added slowly. Stirring was continued in the dark for approximately 10 min after addition. At this time an infrared spectrum of the solution showed the absence of the azide asymmetric stretching band. In the case of the copper azide complexes a clear yellow solution resulted; the solutions containing the silver and gold complexes were colorless. Slow precipitation of the CS_2 adducts was accomplished by partially evaporating the chloroform and adding diethyl ether. The CS_2 adduct of the Au(I) complex was precipitated from an acetone–water mixture.

Preparation of the 5-Perfluoromethyltetrazolato Complexes.—A chloroform solution containing 2 mmol of the azidotriphenylphosphine complexes of Cu, Ag, or Au was cooled to 0° and stirred while trifluoroacetonitrile was bubbled through the solution at 1 atm for approximately 5 min. The reaction mixture was tested for completion by observing the absence of the asymmetric stretching band of the azide. During the formation of the Cu and Au complexes the colorless solution turned to pale yellow. Partial evaporation of the solvent followed by the addition of *n*-hexane caused precipitation of white crystalline material for the copper and silver complexes. In the case of the gold complex, the reaction mixture was evaporated to dryness. The complex was redissolved in acetone and precipitated as white crystalline needles by the addition of a mixture of distilled water and ethanol. The Cu and Ag complexes were recrystallized from a chloroform–*n*-hexane mixture; the recrystallized Au complex was obtained by slowly cooling a saturated $CHCl_3$ solution of the complex from 20° to 0°.

Photochemical Preparation of the Thiocyanato Complexes from the Corresponding CS_2 Adducts.—CS_2 (0.011 mol) in chloroform was added to a chloroform solution containing 0.01 mol of the desired azido complex. The formation of the CS_2 adduct was considered complete when the infrared spectrum of the above solution showed the absence of the azide asymmetric stretching band (2000–2100 cm^{-1}). This solution was then photolyzed under argon until the ir band which is attributed to the thiocarbonyl group (1200 cm^{-1}) had disappeared. The colloidal sulfur was filtered off and the thiocyanato complex which is soluble in chloroform was isolated and recrystallized from a chloroform–hexane solution. The thiocyanato complexes could also be obtained from the isolated CS_2 adducts if the appropriate phosphine was added in a 1:1 ratio to the reaction mixture prior to the photolysis.

Photolysis of ML_2N_3 ($L = P(C_6H_5)_3$; M = Cu(I), Ag(I)), and $AuLN_3$.—Solutions approximately 10^{-2} *M* in the desired complex were irradiated for 1–2 hr. The photolysis reaction mixture was filtered through a medium porosity sintered-glass filter and reduced by evaporation to half-volume. The reaction mixture was then treated with ether and *n*-hexane. The resulting precipitate was collected and recrystallized several times by slow evapo-

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TABLE I
ANALYTICAL DATA FOR GROUP Ib METAL COMPLEXES

Compound	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found	% P Calcd	% P Found
$Cu(P(C_6H_5)_3)_2N_3$	185 dec	68.5	68.3	4.8	4.8	6.7	6.3	9.8	9.6
$Ag(P(C_6H_5)_3)_2N_3$	170 dec	64.1	63.9	4.5	4.4	6.2	6.4	9.2	9.1
$Au(P(C_6H_5)_3)N_3$	190 dec	43.2	43.2	3.0	3.4	8.4	8.1	6.2	6.3
$Cu(P(o\text{-}CH_3C_6H_4)(C_6H_5)_2)_2N_3$	145 dec	69.5	69.4	5.2	4.9	6.4	6.4	9.5	9.6
$Ag(P(o\text{-}CH_3C_6H_4)(C_6H_5)_2)_2N_3$	160 dec	65.1	64.2	4.8	4.6	...	...	8.8	8.9
$Cu_2(diphos)_3(N_3)_2$	160 dec	66.6	66.2	5.2	5.3	...	...	13.3	12.8
$Ag_2(diphos)_3(N_3)_2 \cdot 2DMF$	230 dec	61.0	60.9	5.3	5.5	6.8	6.2	11.3	11.2
$Ag(P(CH_3O)(C_6H_5)_2)_2N_3$	232 dec	42.7	43.0	3.6	3.7	7.3	7.2	8.5	8.8
$Cu(PCH_3(C_6H_5)_2)_2N_3$	160 dec	61.7	61.6	5.0	5.1	...	...	12.3	12.2
$Cu(P(C_6H_5)_3)_2NCS$	230–232	68.8	68.3	4.6	4.5	2.2	2.0	9.6	8.9
$Ag(P(C_6H_5)_3)_2NCS$	225–228	64.3	63.7	4.4	4.6	2.0	2.6	8.9	8.5
$Cu(PCH_3(C_6H_5)_2)_2NCS$	185	62.1	61.8	4.9	5.2	...	...	...	...
$Cu(P(C_6H_5)_3)N_3 \cdot CS_2$	85 dec	51.4	50.8	3.4	3.5	9.5	9.2	7.0	6.3
$Ag(P(C_6H_5)_3)_2N_2 \cdot CS_2$	80 dec	59.0	59.3	4.0	4.1	5.6	5.8	8.3	8.2
$Au(P(C_6H_5)_3)N_3 \cdot CS_2$	95 dec	39.5	38.7	2.6	2.5	...	...	...	...
$Cu(P(o\text{-}CH_3C_6H_4)(C_6H_5)_2)N_3 \cdot CS_2$	90 dec	52.5	51.9	3.7	9.2	...	...	6.8	7.2
$Ag(P(o\text{-}CH_3C_6H_4)(C_6H_5)_2)_2N_3 \cdot CS_2$	90 dec	60.0	59.9	4.4	4.3	...	...	7.9	8.2
$Cu_2(diphos)_3(N_3)_2 \cdot 2CS_2$	82 dec	61.6	61.2	4.6	4.8	...	...	13.1	12.9
$Cu(P(C_6H_5)_3)_2N_3 \cdot CF_3CN$	225–227	63.1	63.1	4.2	4.0	7.7	7.5	8.6	8.3
$Ag(P(C_6H_5)_3)_2N_3 \cdot CF_3CN$	230–232	59.4	59.2	3.9	3.8	7.3	7.2	8.0	7.8
$Au(P(C_6H_5)_3)N_3 \cdot CF_3CN$	200	40.2	41.6	2.5	2.6	9.4	8.9	5.2	5.5

ration from chloroform–ether mixtures. For the photolysis reaction mixture of $Au(P(C_6H_5)_3)N_3$, the mixture was filtered to remove metallic gold which was sometimes present and evaporated almost to dryness. The final product was crystallized from acetone–water mixtures.

II. Thermal and Photolytic Decomposition of $Cu(P(C_6H_5)_3)N_3 \cdot CS_2$. a. Photolysis Products.—Yellow $Cu(P(C_6H_5)_3)N_3 \cdot CS_2$ was prepared as described previously and dissolved in $CHCl_3$ to give a solution approximately 0.05 *M*. The solution was photolyzed in a Vycor vessel as described earlier. The resulting cloudy yellow solution was filtered to remove the suspended material which was shown to be CuNCS. The light yellow filtrate was evaporated and the residue chromatographed on an alumina column. The product was identified as triphenylphosphine sulfide.[10]

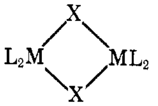
b. Thermolysis Products.—A solution of the yellow adduct was prepared as in part a and refluxed in the dark for about 6 hr. The resulting solution was analyzed as above and was found to contain the same products as in the photolysis reaction.

Thermolysis of $Cu(P(C_6H_5)_3)N_3 \cdot CS_2$.—Thermolysis was carried out on this compound which was prepared by two different methods: one involved addition of CS_2 to a chloroform solution of $Cu(P(C_6H_5)_3)_2N_3$ in a mole ratio of 1:1, and the other involved the addition of $P(C_6H_5)_3$ in a 1:1 mole ratio to a chloroform solution containing $Cu(P(C_6H_5)_3)N_3 \cdot CS_2$. The results are identical in both cases. Typically, 4 mmol of $Cu(P(C_6H_5)_3)_2N_3$ (2.5 g) was added to approximately 250 ml of $CHCl_3$; 4 mmol of CS_2 (0.3 g) was added and the resulting yellow solution was refluxed in the dark for 4 hr. At the end of this period light yellow solid (identified as CuNCS) adhered to the flask wall. The solution was decanted. From this solution triphenylphosphine sulfide and $Cu(P(C_6H_5)_3)_2NCS$ were recovered. No sulfur was produced in this reaction.

Results and Discussion

Analytical data for the complexes reported in this paper are given in Table I. All of these compounds are diamagnetic solids and do not conduct in solution. The elemental analysis of the thiocyanato complexes are for the photolytically prepared samples. Thiocyanato complexes prepared metathetically have properties identical to those of the photolytically prepared samples. The azido complexes of Cu(I) and Ag(I) with the diphenylphosphinous acid esters are relatively unstable[11] and considerable decomposition is noted even in sealed tubes under argon. All other azido complexes are very stable, nonexplosive compounds which could be stored for months with no apparent decomposition. This added stability illustrates the effect of coordinated phosphine ligands in stabilizing the heavy metal azides which themselves are notoriously explosive. Thermal gravimetric analyses of these complexes, however, indicate that they decompose upon melting by slowly evolving nitrogen.

In view of the tendency of phosphine complexes of Cu(I) and Ag(I) to attain four-coordination, it is reasonable to suggest that in the solid state the ML_2X ($X^- = N_3^-$, NCS^-) complexes possess dimeric structures similar to those observed for $[Cu(P(C_6H_5)_3)_2N_3]_2$,[12] $[Ag(P(C_6H_5)_3)_2NCS]_2$,[13] and $[Cu(PCH_3(C_6H_5)_2)_2NCS]_2$[14] as shown below. In solution, however, these



($X^- = N_3^-$, NCS^-)

ML_2X complexes appear to be monomeric (Table II), but one cannot rule out the possibility of ligand dissociation as shown in eq 1.[15,16] In this instance,

$$L_2MX_2ML_2 \rightleftarrows L_2MX_2ML + L \qquad (1)$$

number-average molecular weight values coincident with that of the monomer would be obtained. In general, the solution nature of phosphine complexes of group Ib metals is quite complicated as has been shown recently by Muetterties and Alegranti[16] using ^{31}P temperature-dependent nmr techniques. Unlike the halo complexes of Cu(I) with $P(C_6H_5)_3$ which are known to have metal to ligand ratios of 1:1, 1:2, 1:3, 1:4, and 2:3,[17] it is interesting that with N_3^- and NCS^- only the 1:2 type complexes are observed in the solid state, even when prepared under a variety of different conditions.

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TABLE II
MOLECULAR WEIGHT AND INFRARED DATA

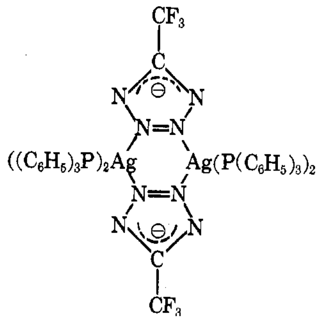
	Mol wt			N–N or N–C asymmetric stretch, cm^{-1}		
Compound	Calcd	Found (CHCl$_3$)	Found (C$_6$H$_6$)	Nujol	CHCl$_3$	C$_6$H$_6$
$Cu(P(C_6H_5)_3)_2N_3$	630	644	. . .[a]	2053	2053	. . .
$Ag(P(C_6H_5)_3)_2N_3$	674	666	. . .	2040	2030	2060
$Au(P(C_6H_5)_3)N_3$	502	504	500	2060	2063	2060
$Cu_2(diphos)_3(N_3)_2$	503	498	. . .	2070	. . .	. . .
$Cu(P(C_2H_5O)(C_6H_5)_2)_2N_3$	563	. . .	557	2090	. . .	. . .
$Cu(P(C_6H_5)_3)_2NCS$	645	. . .	. . .	2097	. . .	. . .
$Ag(P(C_6H_5)_3)_2NCS$	690	700	. . .	2085	2090	. . .
$Au(P(C_6H_5)_3)NCS$	517	496	. . .	2135 (KBr)	. . .	. . .
$Ag(P(C_2H_5O)(C_6H_5)_2)_2NCS$	626	. . .	616	2087	. . .	. . .
					Thiocarbonyl stretch	
$Cu(P(C_6H_5)_3)N_3 \cdot CS_2$	443	440	900 (0.001 M)[b]		1233	
$Ag(P(C_6H_5)_3)_2N_3 \cdot CS_2$	750	745	741		1186, 1195	
$Cu(P(o\text{-}CH_3C_6H_4)(C_6H_5)_2)N_3 \cdot CS_2$	457	464	914 (0.007 M)[b]		1235	
$Cu_2(diphos)_3(N_3)_2 \cdot 2CS_2$	1557	1520	. . .		1232	

[a] Not measured. [b] In monomer.

The copper and silver complexes prepared with the bidentate ligand bis(1,2-diphenylphosphino)ethane (diphos) differed in stoichiometry. Since a reaction between AgCl and diphos could not be detected in CHCl$_3$, hot DMF was used as the solvent. The compound isolated has the novel stoichiometry $(AgN_3)_2$(diphos)$_3 \cdot$2DMF. Recently, the complex $(CuN_3)_2$(diphos)$_3$ was also prepared and an X-ray structural investigation showed the complex to be binuclear with bridging and nonbridging diphos ligands and nonbridging azide ions.[18] It is probable that the silver complex is isostructural with its copper analog.

The infrared asymmetric N$_3$ stretching frequencies of the azido complexes (Table II) fall within the range 2000–2100 cm^{-1}. The value of the N–N asymmetric stretch for discerning the nature of the azide group in the present complexes is questionable. For example, the N–N stretch for $Cu(P(C_6H_5)_3)_2N_3$ is the same in both solution and the solid states. In the solid state this complex is dimeric (*vide supra*), while in solution molecular weight values are coincident with that of a monomer. It is possible, however, as mentioned previously, that the observed molecular weight results from ligand dissociation (eq 1) in which case the bridging structure remains intact.

Addition Products of the Azido Complexes—The addition of CS$_2$ or CF$_3$CN to a chloroform solution of the azido complexes of Cu(I), Ag(I), and Au(I) described above invariably leads to the disappearance of the asymmetric azide stretching band (2000–2100 cm^{-1}) and to the appearance of the characteristic infrared bands for the corresponding five-membered heterocyclic anion that would be formed by the 1,3-dipolar cycloaddition of the azide moiety to the dipolarophiles CS$_2$ and CF$_3$CN. Beck, *et al.*,[6,7,19] originally suggested that the CS$_2$ addition to azido complexes of transition metals occurs at the azide moiety, possibly by a 1,3-dipolar cycloaddition. On the basis of the results described here, this indeed appears to be the case. In most instances the CS$_2$ and CF$_3$CN adducts of the azido complexes could be isolated as crystalline material, and for those adducts characterized (Tables I and II), elemental, thermal gravimetric, and molecular weight analyses suggest the formation of a 1:1 adduct. This conclusion is clearly substantiated by the results of the crystal structure analysis of the CF$_3$CN adducts of $Ag(P(C_6H_5)_3)_2N_3$[20] and $Cu_2(diphos)_3(N_3)_2$.[21] The silver structure is dimeric with bridging tetrazole rings[22] (as depicted below) while in the copper complex the tetrazole ring behaves as a monodentate ligand. The short N–N distance between the two bridging nitrogens (1.200 (5) Å) and the other N–N and N–C distances strongly suggest a localized N–N double bond and delocalization of the negative charge on the N–C–N part of the ring. This is chemically reasonable in view of the presence of the perfluoromethyl group which is a strong electron-withdrawing group. Similar results are observed for the monodentate tetrazole in the copper complex.



The CF$_3$CN adducts are stable both in solution and in the solid state. In solution they show no unusual behavior. The ^{19}F nmr spectra of the complexes $M(P(C_6H_5)_3)_2N_3 \cdot CF_3CN$ (M = Cu(I), Ag(I)) show the perfluoromethyl resonance to occur as a single peak at 7.37 and 8.74 ppm relative to Freon 11 for the copper and silver complexes, respectively. Molecular weight measurements show values slightly higher than those calculated for a monomer indicating either slight association between monomers (assuming cleavage of the dimeric structure) or some dissociation of the dimer to form a 3,4-coordinate complex in a manner suggested earlier.

In contrast to the CF$_3$CN complexes, the yellow CS$_2$ adducts are less stable and can be decomposed either in the solid state or in solution by gentle heating or by the action of light. However, they can be stored in the

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[18] A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chem.*, **10**, 2776 (1971).

[19] W. Beck and W. P. Fehlhammer, *Angew. Chem., Intern. Ed. Engl.*, **6**, 169 (1967).

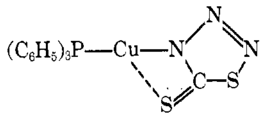
[20] C. G. Pierpont, R. Eisenberg, R. F. Ziolo, A. P. Gaughan, and Z. Dori, to be submitted for publication.

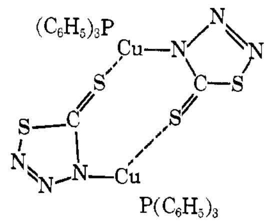
[21] A. P. Gaughan and Z. Dori, submitted to *Inorg. Chem.*

[22] The analogous copper complex is isomorphic and most probably isostructural to the silver complex.

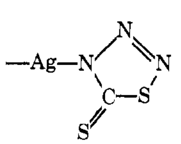
dark at 0° for weeks with no apparent decomposition. The greater stability of the CF_3CN adducts, as is also reflected in their melting points, closely parallels that of organo substituted tetrazoles relative to organic 1,2,3,4-thiatriazole-5-thiols.[23] It is important to note, however, that the thiatriazolato complexes reported here are much more stable than the heavy metal salts of the type $MN_3 \cdot CS_2$ (M = Ag, Au, Hg, and Pb)[24] which are very shock sensitive and may even be detonated under water. The coordination of the tertiary phosphine ligands thus has the same stabilizing effects on these complexes as it does on the heavy metal azides mentioned earlier.

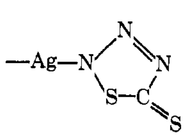
As can be seen from Table I the stoichiometries of the CS_2 adducts of the CuL_2N_3 complexes are unusual in that one of the phosphine ligands is lost. A molecular weight *vs.* concentration study of the yellow copper adducts in $CHCl_3$ reveals monomeric behavior independent of concentration over the range 0.002 *M*–0.12 *M*. In contrast to this, in the nonpolar solvent benzene, the yellow adducts exhibit molecular weights coincident with a dimer (Table II). Since it is unlikely that the copper complex is two-coordinate in $CHCl_3$ solution it is reasonable to suggest that intramolecular sulfur–metal coordination takes place, as shown, resulting in an effectively three-coordinate complex. In nonpolar solvents intermolecular sulfur–metal bonding may become important and one possible structure for the dimer in benzene is depicted below. However, one cannot rule out a structure similar to the one observed for the CF_3CN adduct of $Ag(P(C_6H_5)_3)_2N_3$.[20] Attempts to determine the structure of these unusual complexes were unsuccessful because of their sensitivity to the X-ray beam. In contrast to the copper complexes, the analogous silver complexes do not lose phosphine.





The most characteristic infrared band for these CS_2 adducts is the one near 1200 cm⁻¹ which can be associated with the thiocarbonyl group. This band appears about 100 cm⁻¹ lower in energy than the one observed for organic substituted thiothiatriazoles.[25] It is interesting that the complex $Ag(P(C_6H_5)_3)_2N_3 \cdot CS_2$ exhibits two strong bands at 1195 and 1186 cm⁻¹, and if both bands are associated with the thiocarbonyl stretching their presence may indicate the existence of two isomers as illustrated below. Attempted separations of these possible isomers by chromatography were unsuccessful.





Decomposition of the CS_2 Addition Products.—When a chloroform solution containing $Cu(P(C_6H_5)_3)_2N_3$ and CS_2 in a 1:1[26] mole ratio is photolyzed in a Vycor vessel the corresponding thiocyanato complex can be isolated. During the reaction N_2 is liberated and colloidal sulfur is deposited. Quantitative analysis of N_2, sulfur, and the thiocyanato complex clearly suggests that the reaction can be written as shown by eq 2.

$$\mathrm{Cu(P(C_6H_5)_3)_2N_3 + CS_2 \xrightarrow[CHCl_3]{h\nu} Cu(P(C_6H_5)_3)_2NCS + S + N_2} \qquad (2)$$

The photolysis of the other CS_2 adducts of Cu(I) and Ag(I) reported here leads to the same results.

When the above solution is refluxed in the dark, thermal decomposition of the thiothiatriazolato complex takes place and this is summarized in eq 3.

$$\mathrm{2Cu(P(C_6H_5)_3)_2N_3 + CS_2 \xrightarrow{CHCl_3} CuNCS + Cu(P(C_6H_5)_3)_2NCS + 2(C_6H_5)_3PS + 2N_2} \qquad (3)$$

Quantitative amounts of $(C_6H_5)_3PS$ were recovered. It is thus clear that the thermal decomposition is more complicated than the photochemical reaction and probably proceeds by a different route.

Earlier we have noted[7] that when the complex $Cu(P(C_6H_5)_3)N_3 \cdot CS_2$ is photolyzed in $CHCl_3$ under the same conditions as previously mentioned, one obtains different products from those depicted in eq 2. Indeed, when the above complex is decomposed photolytically or thermally, in the absence of $P(C_6H_5)_3$, polymeric CuNCS and triphenylphosphine sulfide are formed according to eq 4.

$$\mathrm{Cu(P(C_6H_5)_3)N_3 \cdot CS_2 \xrightarrow{CHCl_3} CuNCS + (C_6H_5)_3PS + N_2} \qquad (4)$$

Stoichiometric amounts of CuNCS,[27] triphenylphosphine sulfide, and N_2 are obtained. The reaction proceeds analogously to the slow thermal decomposition of the alkali metal thiothiatriazole salts,[28] only in the present case triphenylphosphine sulfide is formed instead of sulfur. In addition, we note that the yellow color of the CS_2 adducts can be dispelled easily by the addition of excess phospine such as $P(n\text{-}C_4H_9)_3$, $P(CH_3)_2(C_6H_5)$, or $P(OR)_2C_6H_5$ (R = CH_3, C_2H_5). It is reasonable to suggest that these phosphines attack the thiothiatriazole moiety and abstract a sulfur atom from the ring. Indeed, a vacuum distillation of a colorless mixture of $Cu(P(C_6H_5)_3)N_3 \cdot CS_2$ and excess $P(n\text{-}C_4H_9)_3$ yields $(n\text{-}C_4H_9)_3PS$. This type of reaction is well documented.[29]

Photochemical Decomposition of CuL_2N_3, AgL_2N_3, and $AuLN_3$ (L = $P(C_6H_5)_3$).—The photolysis of a

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[23] K. A. Jensen and C. Pedersen, *Advan. Heterocycl. Chem.*, **3**, 263–284 (1964).

[24] G. B. L. Smith, P. Warttman, and A. W. Browne, *J. Amer. Chem. Soc.*, **52**, 2806 (1930).

[25] E. Lieber, V. N. Pillai, J. Ramachandran, and R. D. Hites, *J. Org. Chem.*, **22**, 1750 (1957).

[26] This solution can also be prepared from addition of $P(C_6H_5)_3$ in a 1:1 mole ratio to a chloroform solution containing $Cu(P(C_6H_5)_3)N_3 \cdot CS_2$.

[27] CuNCS was identified through its reaction with $P(C_6H_5)_3$ which leads to the formation of thiocyanatobis(triphenylphosphine)copper(I).

[28] L. F. Audrieth, *Chem. Rev.*, **15**, 169 (1934).

[29] P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, **78**, 3710 (1956).

chloroform solution containing the above-mentioned complexes invariably leads to the decomposition of the azide and to the formation of the following complexes: $Cu_2L_3Cl_2$, $[AgLCl]_4$, and AuLCl. It should be noted that $CHCl_3$ itself does not undergo photochemical decomposition under the same conditions.[30] Mass spectral analysis of the gaseous products obtained from the photolysis of CuL_2N_3 indicates the products to consist of over 98% N_2. Small amounts of CO_2, O_2, and H_2 are also present and their source is currently being studied.[31] Quantitative nitrogen analysis showed that the decomposition produced nitrogen in 85% yield based on 100% yield for the complete conversion of azide to nitrogen. The remaining nitrogen was accounted for as hydrazoic acid which was obtained in the forerun of the distillation of the photolyzed solution.

The decomposition of transition metal azides to produce nitrogen has been interpreted to proceed either by homolytic cleavage of the metal–nitrogen bond[32] or by cleavage of the N–N bond of the azide resulting in the formation of a metal–nitrene intermediate.[3] From the evidence available to us to date it appears that the photolysis leads to homolytic cleavage of the copper–nitrogen bond resulting in the formation of azide radicals and a Cu(0) complex which then react with the solvent.[30] However, we cannot rule out the second possibility since we have failed to detect any volatile compounds other than $CHCl_3$, C_2H_5OH, and HN_3. This interesting reaction is currently being investigated in detail.

Acknowledgment—We wish to thank Professor R. Eisenberg for helpful discussions and the National Science Foundation for financial support. We also thank Nina Ziolo and Robert Coldwell of Sadtler Research Laboratories for their cooperation.

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[30] During the reaction we note the buildup of an intense purple color in solution. Spectral measurements indicate the maximum to be centered at 5400 Å with a shoulder at around 4600 Å. The solution also appears to be paramagnetic and this will be reported at a later date.

[31] One possible source for these gases is the ethanol which is present as an inhibitor in chloroform.

[32] V. Balzani, L. Maggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta Rev.*, **1**, 7 (1967).

Contribution from the Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514

The Electrochemical Oxidation of 1,2-Bis(diphenylphosphino)ethanebis(π-cyclopentadienylcarbonyliron)

By JOHN A. FERGUSON and THOMAS J. MEYER*

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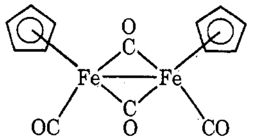
The electrochemical oxidation of the metal–metal bond in the carbonyl-diphosphine bridged dimer $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (Ph = C_6H_5) (I) in a variety of solvents occurs by two one-electron steps. The removal of the first electron to give the cation $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ (II) is electrochemically reversible in all media studied. Compound II is apparently isostructural with I and contains a "one-electron" metal–metal bond. Removal of a further electron from II in acetonitrile gives two kinds of reaction products by separate reaction paths. The product from one path is the diphosphine-bridged acetonitrile complex $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV) which arises from symmetrical cleavage of the molecule after complete oxidation of the metal–metal bond, and in the other, unsymmetrical cleavage gives the unidentate diphos complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ (III) and Fe^{2+}. The relative importance of the two paths depends upon the solvent and the temperature. In acetonitrile, II disproportionates with a half-time of 30 ± 5 min at 22 ± 2° to give $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)$ (I) and $\{[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2PCH_2CH_2PPh_2)\}^{2+}$ (IV).

Introduction

Haines and Du Preez have reported the preparations of the bridged diphosphine complexes $[(\pi\text{-}C_5H_5)Fe(CO)]_2[Ph_2P(CH_2)_nPPh_2]$ (n = 1, 2, 3).[1] From infrared and nmr data the structures of the complexes are as shown in Figure 1 where 1,2-bis(diphenylphosphino)ethane (n = 2) is the bridging ligand.

The complexes are oxidized by iodine in benzene solution.[2] Equimolar iodine gives the cations $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2[Ph_2P(CH_2)_nPPh_2]\}^+$ in which a single electron has been lost giving a "one-electron metal–metal bond" and the bridging carbonyls and diphosphine remain intact. Oxidation of either $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2CH_2CH_2PPh_2)$ or $\{[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2PCH_2CH_2PPh_2)\}^+$ by excess iodine gives the unidentate diphos complex $[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_2PCH_2CH_2PPh_2)]^+$ as the major product.

We recently reported that electrochemical oxidation of the metal–metal bond in the related iron carbonyl dimer



occurs by a two electron transfer step and that oxidation proceeds with symmetric cleavage of the molecule[3]

$$2S + [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \xrightarrow{-2e^-} 2[(\pi\text{-}C_5H_5)Fe(CO)_2S]^+ \quad (S = CH_3CN, (CH_3)_2CO)$$

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[1] R. J. Haines and A. L. Du Preez, *J. Organometal. Chem.*, **21**, 181 (1970).

[2] R. J. Haines, A. L. Du Preez, and G. T. W. Wittmann, *Chem. Commun.*, 611 (1968).

[3] J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, **10**, 1025 (1971).