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New Azide Bridged Metal Complexes, $[Au(CH_3)_2N_3]_2$ and $[(C_6H_5)_3PPd(N_3)_2]_2$[1]

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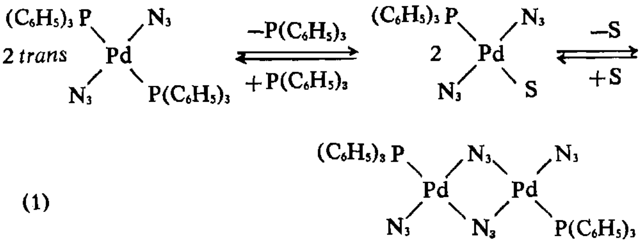
Monomeric $[(C_6H_5)_3P]_2Pd(N_3)_2$ reacts in certain solvents and even in the solid state to yield the dimer $[(C_6H_5)_3PPd(N_3)_2]_2$. This compound which has both bridging and terminal azides shows out-of-phase azide stretching frequencies at 2075 (bridge) and 2027 cm^{-1} (terminal). Dimethylgold(III) azide has been synthesised and found to be dimeric. The skeletal vibrations of this compound which contains only bridging azides have been assigned on the basis of D_{2h} symmetry. Only one infrared active out-of-phase azide stretching mode at 2088 cm^{-1} is observed. The complete infrared spectra of these compounds (35-4000 cm^{-1}) are reported.

Introduction

Previously we have described some transition metal azide complexes in which azide-bridges have to be presumed to exist.[2] These compounds, *e.g.* $[Pd_2(N_3)_6]^{2-}$, show in their infrared spectra two *intense* antisymmetric azide stretching frequencies, whereas in the monomeric complexes only one intense $\nu_{as}(N_3)$ absorption for the terminal azide ligands is observed. However the frequency of the band which was assigned to the azide bridges lies only slightly higher than the corresponding stretching mode of monomeric compounds. For an unambiguous assignment of the infrared absorptions of the azide-bridges we have been interested in other azide-bridged transition metal complexes.

Results and Discussion

It has been found that the colour of a solution of the monomeric yellow palladium-complex *trans*-$[(C_6H_5)_3P]_2Pd(N_3)_2$[2] in tetralin rapidly changes to dark-red on heating (60-100°). On adding petroleum-ether/ether to the hot solution dark-red crystals with the formula $[(C_6H_5)_3PPd(N_3)_2]_2$ are obtained. The dimeric structure of the compound was established by analyses and molecular weight determination. It is worth mentioning that the formation of this product strongly depends on the solvent used. Dimerisation has been found to occur also in nitrobenzene (100°) and boiling bromobenzene but not in benzene and toluene. In order to form an azide bridge a palladium-phosphine-bond must be broken; we assume that in the first step a triphenylphosphine ligand is substituted by a solvent molecule. The low dipole moment[3] of the azide bridged complex (μ = 1.5 D in benzene) indicates, that the trans-symmetric isomer is formed (Equation 1).



(1)

(S = solvent)

In tetralin solution there exists (1) an equilibrium between the monomeric and the binuclear compound. If the red solution in tetralin is cooled very slowly, the orange-yellow starting material is reobtained; the azide bridges also are split by adding an excess of triphenylphosphine to the dimeric compound. In the presence of $P(C_6H_5)_3$ higher temperatures are necessary for the formation of the dimeric complex. The compounds $[C_6H_5)_3PPd(N_3)_2]_2$ and $[(C_6H_5)_3P]_2Pd(N_3)_2$ show identical decomposition points, and the latter turns red on heating. These observation indicate, that dimerisation also occurs in the solid state.

Di-μ-azido-bis(azido-triphenylphosphine-palladium(II)) corresponds to the analogous compounds with halide-,[4] SCN-,[4] or sulfur-[5] bridges. It is remarkable that all these dimeric complexes are of red to orange-red colour in contrast to the yellow monomeric complexes.[4,5]

The solid state infrared spectrum of $[(C_6H_5)_3PPd(N_3)_2]_2$ contains two intense $\nu_{as}(N_3)$ stretching bands at 2075 and 2027 cm^{-1}. Similar frequencies have

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[1] Pseudohalogenometal complexes XXVI; XXV: W. Beck, H. Werner, H. Engelmann und H. S. Smedal, *Chem. Ber. 101*, 2143 (1968).

[2] W. Beck, W. P. Fehlhammer, P. Pöllmann, E. Schuierer und K. Feldl, *Chem. Ber. 100*, 2335 (1967).

[3] Solution of the compound in benzene at 40° showed a higher dipole moment (μ = 2.8 D) (*trans-cis* isomerisation?). We thank Prof. H. Nöth, Universität Marburg, for measuring the dipole moments.

[4] F. G. Mann and D. Purdie, *J. Chem. Soc.* 873 (1936); J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 2351 (1957).

[5] J. Chatt and F. A. Hart, *J. Chem. Soc.* 2807 (1960); 2363 (1953); W. Beck, K. H. Stetter, S. Tadros und K. E. Schwarzhans, *Chem. Ber. 100*, 3944 (1967).

been found for the dimeric $[Pd_2(N_3)_6]^{2-}$ (Table II), and the higher frequencies are assigned to the azide bridges. In contrast to these palladium complexes, in the azide-bridged compounds of boron, aluminum and antimony, *e.g.* $(BCl_2N_3)_3$,[6] $(Al(C_2H_5)_2N_3)_3$,[7] and $(SbCl_4N_3)_2$,[8] the $\nu_{as}(N_3)$ bands appear at relatively high frequencies ($\sim$2200 cm^{-1}).

The compounds described so far contain terminal and bridged azide groups attached to the same metal, whereas in dimethylgold azide only azide bridges have to be present in order to get the preferred coordination number four for the central gold(III)-atom. Compounds of the type $[R_2AuX]_n$ where X=Cl,Br, n=2 and X=CN,OH,[9] n=4 are well known;[10] recently their vibration spectra have been studied.[9]

Dimethylgold azide is prepared from dimethyl(ethylenediamine)goldiodide and silver azide by treating the $[Au(CH_3)_2en]N_3$ with hydrochloric acid in aequous solution.

$$[(CH_3)_2Au\ en]I + AgN_3 \rightarrow [(CH_3)_2Au\ en]N_3 + AgI$$

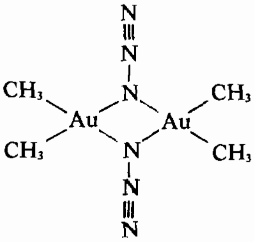
$$2[(CH_3)_2Au\ en]N_3 + 2HCl \rightarrow [(CH_3)_2AuN_3]_2 + 2enH^+Cl^-$$

The colourless dimethylgold azide proved to be extremely explosive and was therefore prepared only in very small quantities. Even under water it can detonate if touched.

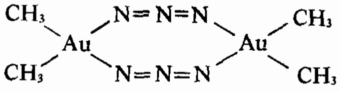
Its dimeric structure, which is found also in the corresponding halide compounds, was confirmed by molecular weight measurements. The ^{1}H n m r spectrum exhibits only a single sharp methyl signal, showing that the four methyl groups are equivalent. This is consistent with a planar structure for the molecule.

For a tetrameric structure two methyl proton signals of the same intensity should appear as it was found for $[(CH_3)_2AuOH]_4$ due to the axial and equatorial methyl groups.[11] The dimeric thiocyanate compound $[(CH_3)_2AuNCS]_2$ [12] which contains Au-N-C-S-Au bridges also gives two p m r methyl signals.

For dimethylgold azide the following two structures I and II are possible



I



II

Both structures have D_{2h} symmetry; one therefore cannot decide from the number of the infrared active vibrations or from the ^{1}H n mr spectrum between these different types of azide bridges.

The infrared spectrum of dimethylgold azide was recorded in the range 35-3500 cm^{-1}. In Table I the observed bands are listed together with their assignments, assuming structure I. In the D_{2h} point group 14 infrared active fundamentals

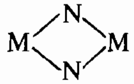
$$\Gamma = 6A_g + B_{1g} + 3B_{2g} + 5B_{3g} + A_u + 5\mathit{B}_{1u} + 5\mathit{B}_{2u} + 4\mathit{B}_{3u}\ ^{13}$$

are expected for the skelet $[C_2AuN_3]_2$.

The most obvious feature of the spectrum is the appearance of only one $\nu_{as}(N_3)$ out-of-phase stretching mode (B_{1u}) at 2088 cm^{-1}. From this result, the relatively low frequencies of the $\nu_{as}(N_3)$-bands of azide bridges in transition metal complexes and the assignment which we have made for the dimeric complex $[Pd_2(N_3)_6]^{2-}$ is substantiated.

Recently Dehnicke and Müller[14] described the compounds $(Ga(C_2H_5)_2N_3)_3$ and $(In(C_2H_5)_2N_3)_2$ with six- and four-membered ring structures which also show $\nu_{as}(N_3)$ bands of the azide-bridges at 2080-2100 cm^{-1}.

The γ and δ N_3^- bending modes ($B_{2u}+B_{3u}$) appear in a characteristic frequency range (719, 709, 632 cm^{-1}, m) which is not covered by other bands (CH_3).

Two infrared active ν,δ-ring modes ($B_{1u}+B_{2u}$) arise from the motion of the four membered ring  (Table I and II)) with local D_{2h} symmetry. This ring also occurs in compounds like $(Cl_4SbN_3)_2$ [8] and $(SnCl_2(N_3)_2)_n$.[15] The bands of dimethylgold azide at 396(sh) and 420 cm^{-1} which we assign to these ring-vibrations[16] may be qualitatively considered as localized Au-N-stretching vibrations. They appear at similar wavenumbers as in the related $[Au(N_3)_4]^-$-complex (νAu–N=432 cm^{-1}). The assignments of the bands at 572,563(sh) and 257 cm^{-1} to the AuC_2 stretching and bending vibrations is unambiguously substantiated by comparison with the corresponding absorptions of dimethylgold(ethylenediamine)iodide.[9] The remaining bands at 284,233,150 and 137 cm^{-1} may be assigned to the expected γ,δAuNN and γ,δCAuN bending vibrations as well as to the γ-ring vibration.

The infrared spectrum of $[(C_6H_5)_3PPd(N_3)_2]_2$ exhibits two $\nu_{as}(N_3)$ and $\nu_s(N_3)$ bands for the terminal and the bridging azide groups. This is an agreement with a structure of point group C_{2h} (sym-trans), whereas for a structure with cis-$P(C_6H_5)_3$-ligands (symmetry C_{2v}) ($\nu_{as}N_3'$, ν_sN_3': 4(A_1); $\nu_{as}N_3$,ν_sN_3: 4(A_1+B_1))$^{17)}$ four $\nu_{as}(N_3)$ and $\nu_s(N_3)$ bands are to be expected.

The metal-phosphorus-stretching-frequency appears

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(6) P. I. Paetzold, M. Gayoso und K. Dehnicke, *Chem. Ber. 98*, 1173 (1965).

(7) K. Dehnicke, J. Strähle, D. Seybold und J. Müller, *J. Organometal, Chem. 6*, 298 (1966).

(8) N. Wiberg und K. H. Schmid, *Chem. Ber. 100*, 741 (1967); U. Müller und K. Dehnicke, *Z. anorg. allg. Chem., 350*, 113 (1967).

(9) M. G. Miles, G. E. Glass and R. S. Tobias, *J. Amer. Chem. Soc., 88*, 5738 (1966).

(10) G. E. Coates, Organometallic Compounds, Methuen, London 1956.

(11) G. E. Glass, J. H. Konnert., M. G. Miles, D. Britton and R. S. Tobias, *J. Amer., Chem. Soc. 90*, 1131 (1968).

(12) R. S. Tobias, unpublished work.

(13) The italic representations belong to infrared active modes (σ_{yz} = plane of molecule, z = axis pointing towards the nitrogen atoms). The coordinate system was chosen according to *J. Chem. Phys., 23*, 1997 (1955).

(14) J. Müller und K. Dehnicke, *J. Organometal, Chem., 12*, 37 (1968).

(15) N. Wiberg und K. H. Schmid, *Chem. Ber., 100*, 748 (1967).

(16) The assignments of the ring vibrations differ in (14) and (15).

(17) In the point group C_{2v}, the in phase N_3-vibrations (A_1) also are infrared active.

at rather low wavenumbers(18). The assignment of the bands of the triphenyl-phosphine ligand was made according to Whiffen(19) and Deacon and Green(20).

Table I. IR-Frequencies (cm^{-1}) of $[(CH_3)_2AuN_3]_2$ (in nujol and hostaflon mull).

ν[cm^{-1}]	Assignment	
2993 vw	$\nu_{as}CH_3$	
2921 vw	ν_sCH_3	
2488 vw	comb.-vibr.	
2087 ^{a} vs	$\nu_{as}N_3$	$1(B_{1u})$
1419 vw	$\delta_{as}CH_3$	
1279 w-m	ν_sN_3	$1(B_{1u})$
1255 1213 } s	δ_sCH_3	
1142 vw	?	
805 m(b)	ρCH_3	
719 m-s		
709 m	$\delta,\gamma N_3$	$2(B_{2u}+B_{3u})$
632 m		
572 m, 563 (sh)	νAuC_2	$2(B_{1u}+B_{2u})$
420 s, 396 (sh)	ν,δ-ring	$2(B_{1u}+B_{2u})$
284 w(sh)	?	
257 w	δAuC_2	$1(B_{2u})$
233 w, 150 w(b)	$\gamma,\delta AuNN$	
137 w	$\gamma,\delta CAuN$ γ-ring?	$1(B_{1u})+1(B_{2u})+3(B_{3u})$

^{a} In $CHCl_3$: $\nu_{as}N_3$ 2088 vs.

Further studies on organogold and also organoplatinum(IV) azides are in progress.

Experimental Section

Di-μ-azido-diazido-bis(triphenylphosphine)-dipalladium(II): 1 g of $[(C_6H_5)_3P]_2Pd(N_3)_2$ (1,4 mmole) was partially dissolved in 20 ml of freshly distilled tetralin under a nitrogen atmosphere in a Schlenk-tube. The solution was quickly heated by putting it into an oil-bath at 100°. Immediately a dark red solution was obtained from which the dimeric compound precipitates on adding a mixture of ether and petroleum-ether. It is important that the product be isolated at once; prolonged heating leads to decomposition (under gas evolution and formation of a dark solid). The product was recrystallised from CH_2Cl_2 adding ether and petroleumether (decomp-point 182°). The dark red crystals are readily soluble in CH_2Cl_2, chloroform and acetone, while they are only slightly soluble in benzene.

$[(C_6H_5)_3P]_2Pd_2(N_3)_4$ Molecular weight. Calcd. 905.5 Found 900 (by vapor pressure osmometer using $CHCl_3$).

Table II IR-Frequencies (cm^{-1}) of $[Ph_3PPd(N_3)_2]_2$ ($Ph=C_6H_5$) and Triphenylphosphine (in KBr and nujol)

$[AsPh_4]_2$ $[Pd(N_3)_4]$	$[AsPh_4]_2[Pd_2(N_3)_6]$ D_{2h}		$[Ph_3PPd(N_3)_2]_2$ ^{a} C_{2h}	PPh_3^{a}	Assignment
	2060 vs	$1(B_{1u})$	2075 vs $1(B_u)$		$\nu_{as}N_3'$ ^{b}
2017 vs	2033 2000 } vs	$2(B_{1u}+B_{2u})$	2027 vs $1(B_u)$		$\nu_{as}N_3$
1281 m-s	1283 m	$2(B_{1u}+B_{2u})$	1283 s $1(B_u)$		ν_sN_3
	1271 m	$1(B_{1u})$	1269 s $1(B_u)$		ν_sN_3'
			1098 vs $1(B_u)$	1089 vs	qX-sens.PPh_3
			713 m-s		rX-sens.PPh_3
			693,585 vs	697 vs	v∅(CC)PPh_3
			614 w	617 w	sα(CCC)PPh_3
590 w	583 } w	$3(B_{1u}+B_{2u}+B_{3u})$	572 vw $2(A_u+B_u)$		$\gamma,\delta N_3$
	563	$2(B_{2u}+B_{3u})$	563 w $2(A_u+B_u)$		$\gamma,\delta N_3'$
				540 w	
			535 vs	513 s	
			512 vs	496 vs	yX-sens.PPh_3
			504 (sh)	490 (sh)	
			458 w-m	433 422 } m	tX-sens.PPh_3
449 w-m			423 m		
			401 (sh)	398 w	w∅(CC)PPh_3
398 s(b)	417 403 } s	$2(B_{1u}+B_{2u})$	393 m $1(B_u)$		νPd-N
	300 m	$2(B_{1u}+B_{2u})$	294 m-s(b)$2(B_u)$		ν,δ-ring
			277 vw	271 w	
				254 m 246 m }	uX-sens.PPh_3
223 m(b)	227 s	$3(B_{1u}+B_{2u}+B_{3u})$	$2(A_u+B_u)$		$\gamma,\delta PdNN$
205 w(b)	220 (sh)				
	150 m	$2(B_{2u}+B_{3u})$	$2(A_u+B_u)$		$\gamma,\delta PdN'N'$
			215 w	215 m	
			196 vw	196 m	PPh_3
				185 w	
			132 w(vb)$1(B_u)$		νPd-P ?
			117 w	116 87 } w	PPh_3
	74 w	$1(B_{1u})+1(B_{2u})+2(B_{3u})$	98 w $3(A_u)+2(B_u)$		γ-ring ? $\gamma,\delta NPdN(N')$ $\gamma,\delta PPdN(N')$

^{a} The phenyl vibrations above 700 cm^{-1} are not listed in the Table. ^{b} N′ = bridging azide.

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(18) G. B. Deacon und J. H. S. Green, *Chem. Commun. 1966*, 629; J. Bradbury, K. P. Forest, R. H. Nuttall und D. W. A. Sharp, *Spectrochim. Acta, 23A*, 2701 (1967).

(19) D. H. Whiffen, *J. Chem. Soc.* 1350 (1956).

(20) G. B. Deacon und J. H. S. Green, *Spectrochim. Acta, 24A*, 845 (1968).

Analysis

Calcd.	C 47.75	H 3.34	N 18.56	Pd 23.50
Found	C 47.86	H 3.84	N 18.73	Pd 23.69

Dimethylgoldazide: 0,2 g of dimethyl(ethylenediamine)gold(III)-iodide (0,5 mmole) was dissolved in water. After addition of 0.2 g of wet silver azide, the mixture was shaken in a polyethylene tube for 1/2 hour. Silver iodide and the excess of silver azide was filtered off. The clear filtrate was evaporated to 10 ml under a water aspirator vacuum at 40°. Dilute HCl was dropped slowly into the solution until a white precipitate was obtained. The product was carefully filtered off, washed with water and airdried in darkness. The dry compound is very explosive and sensitive to touch; it therefore was not possible to get an analysis of the compound. It is soluble in chloroform and pyridine (giving a complex).

$[(CH_3)_2AuN_3]_2$ Molecular weigth. Calcd. 538.0 Found 556 (vapor pressure osmometer using $CHCl_3$) p m r spectrum: τ 8,8 (in $CDCl_3$).

The infrared spectra were run with a Perkin-Elmer-spectrometer Mod. 21 with NaCl optics and with a Beckman IR 11.

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