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Preparation and Reactivity of Some New Azido-bridged Complexes of Pd(II) and Pt(II)

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Azido-bridged complexes of Pt(II) and Pt(II) of the type $[(dieneOCH_3)MN_3]_2$ *(M = Pd, Pt) and* $[(\pi\text{-}allyl)PdN_3]_2$ *have been prepared by methathetical reaction from their chloro-bridged congeners. The bridging azido group in these new complexes reacts with carbon monoxide to give the corresponding cyanato-bridged complexes, whereas with* CS_2, CF_3CN *and* $SCNC_6H_5$ *undergoes 1,3-cycloaddition to form thiatriazolate or tetrazolate groups bridging in dimeric complexes of the type* $[(dieneOCH_3)M(N_3CS_2)]_2$ *(M = Pd, Pt),* $[(\pi\text{-}allyl)Pd(N_3CS_2)]_2$, $[(\pi\text{-}allyl)Pd(N_3CF_3CN)]_2$ *and* $[(\pi\text{-}allyl)Pd(N_3SCNC_6H_5)]_2$.

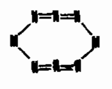
Preliminary results on the termal decomposition of the CS_2 *adducts and on the reaction with COS are reported and discussed.*

Introduction

Although the study of the reactivity of the terminal azido groups bonded to transition metals has received increased interest in the past several years[1], only little work has been done on the reactivity of the bridging azido group.

It is known that the azide group (N_3^-) can act as a bidentate ligand bridging metals in various polymeric metal azides. Two bridging modes are available for the azide anion (A and B).

A



B

Mode A is examplified in the structures of $[(Pd_2(N_3)_6]^{2-}$[2] and $[(CO)_3Mn(N_3)_3Mn(CO)_3]^-$[3], while mode B is examplified in the structure of $[Cu(PPh_3)_2N_3]_2$[4].

In addition the bridging mode of the azide has been suggested on the basis of i.r. spectra to be of type A in complexes of the type $[Au(CH_3)_2N_3]_2$[5], $[Pd(PPh_3)_2(N_3)_2]$[5], $[(PPh_3)_2M(N_3)_2M(PPh_3)_2]^{2+}$ (M = Pd, Pt)[6], $[(diphos)NiN_3]_2^{2+}$[7], and $[(PPh_3)_2(CO)MN_3M(CO)(PPh_3)_2]^+$ (M = Rh, Ir)[6].

In other d^8 metals azido-bridged complexes such as $[(CO)_2RhN_3]_2$[8] and $[\pi\text{-}C_3H_4CH_3PdN_3]_2$[9] both modes A and B have been indicated as possible from analysis of their i.r. spectra.

This paper reports the preparation of new azido-bridged complexes of the type $[(\pi\text{-allyl})PdN_3]_2$ and $[(dieneOCH_3)MN_3]_2$, (M = Pd, Pt; π-allyl = $\pi\text{-}C_3H_5$, $\pi\text{-}C_6H_9$; diene = cycloocta-1,5-diene, cycloocta-1,3-diene, dicyclopentadiene and cyclooctatetraene), by a method that has been used for other analogous complexes of d^8 metals[8,9].

With the aim to compare the reactivity of the bridged azido group with that of the terminal azido group we have carried out some reactions that have been successfully tested for monomeric azido complexes of transition metals, such as reaction with CO and 1,3-dipolar cycloaddition with CS_2, CF_3CN, $SCNC_6H_5$ and COS.

Experimental

Materials

The compounds $[(\pi\text{-allyl})PdCl]_2$ (π-allyl = C_3H_5[10], C_6H_9[11], C_8H_{13}[12] and $[(dieneOCH_3)MCl]_2$ (M = Pd, diene = C_8H_8[11], 1,3-C_8H_{12}[11], 1,5-C_8H_{12}[13], $C_{10}H_{12}$[13]; M = Pt, diene = 1,5-C_8H_{12}, $C_{10}H_{12}$[14]) were synthesized as described in the literature.

Tetrabutylammonium azide[15], trifluoroacetonitrile[16] and the azidedithiocarbonate $Na[CS_2N_3]$[17] were prepared by published methods.

Reagent grade chemicals were used in the preparation of the complexes. All the reactions were carried out under nitrogen.

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Instrumentation

Infrared spectra were recorded on a Perkin–Elmer Model 457 infrared spectrophotometer. Molecular weights were determined by vapor pressure osmometry with a Macrolab Model 302 B. Conductivity measurements were made using a LKB 5300 B conductivity bridge.

Preparation of $[(\pi\text{-allyl})PdN_3)]_2$ (π-allyl = C_3H_5, C_6H_9, C_8H_{13})

The complexes were prepared in an almost quantitative yield by the following procedure. To a solution of 1.0 mmol of $[(\pi\text{-allyl})PdCl]_2$ in 40 ml of acetone a twofold molar excess of tetrabutylammonium azide was added with stirring in a nitrogen atmosphere. After 1 hr the solution was concentrated to a small volume and the crude yellow product was precipitated with water and filtered. The $[(\pi\text{-allyl})PdN_3]_2$ were dissolved in benzene, treated with charcoal, filtered and recrystallized from benzene/pentane.

The $[(\pi\text{-allyl})PdN_3]_2$ complexes are stable in the air in solid state for several weeks but decompose slowly in solution.

Preparation of $[(dieneOCH_3)MN_3]_2$ (M = Pd, diene = C_8H_8, 1,3-C_8H_{12}, 1,5-C_8H_{12}, $C_{10}H_{12}$; M = Pt, diene = 1,5-C_8H_{12}, $C_{10}H_{12}$)

To a suspension of $[(dieneOCH_3)MCl]_2$ (1.0 mmol) in methanol (30 ml), was added a large excess of solid NaN_3. After stirring at room temperature for 3 hr the solid product was filtered, washed with methanol and water and recrystallized from CH_2Cl_2/petroleum ether; yield > 90%.

Reaction of $[(\pi\text{-}C_3H_5)PdN_3]_2$ and $[C_{10}H_{12}OCH_3MN_3]_2$ (M = Pt, Pd) with Carbon Monoxide

Carbon monoxide was bubbled through a CH_2Cl_2 solution of the azido-bridged complexes for 48 hr at room temperature, giving, after concentration to small volume and addition of pentane, the cyanato complexes in an almost quantitative yield. The complexes are air stable, but slowly decompose in solution. The physical and spectroscopic properties of these complexes are identical with authentic samples obtained by metathesis from the dimeric chloride compounds and KNCO in acetone solution at room temperature.

Reaction of $[(\pi\text{-}C_3H_5)PdN_3]_2$ with CF_3CN

Trifluoroacetonitrile was bubbled slowly for 15 hr at room temperature through a stirred CH_2Cl_2 solution (25 ml) of $[(\pi\text{-}C_3H_5)PdN_3]_2$ (0.380 gr, 1 mmol). The reaction mixture was tested for completion by observing the absence of the asymmetric stretching band of the azide. During the formation of 5-perfluoromethyltetrazolato complex $[(\pi\text{-}C_3H_5)Pd(N_3CF_3CN)]_2$ the yellow solution turned colorless. Partial evaporation of the solvent followed by the addition of *n*-hexane caused the precipitation of the white solid $[(\pi\text{-}C_3H_5)Pd(N_3CF_3CN)]_2$ in 80% yield. The product may be recrystallized from CH_2Cl_2/hexane.

Preparation of $[(\pi\text{-}C_3H_5)Pd(N_3CS_2)]_2$ and $[(dieneOCH_3)M(N_3CS_2)]_2$ (M = Pt, diene = $C_{10}H_{12}$; M = Pd, diene = 1,3-C_8H_{12}, 1,5-C_8H_{12}, $C_{10}H_{12}$)

From azido-complexes and CS_2

A solution of 1 mmol of the appropiate azido complex in 20 ml of dichloromethane was treated under nitrogen and in the dark with a large excess of carbon disulfide (~ 2 ml). Stirring was continued for approximately 1 hr and at this time an infrared spectrum showed the absence of the azide asymmetric stretching band. The solution was concentrated to a small volume and addition of hexane followed by filtration gave in an almost quantitative yield the product. It was crystallized from dichloromethane–hexane and dried under vacuum. The complexes decompose in solution while in the solid state are stable for several days under nitrogen and in the dark; they are explosive to the percussion.

From chloro-bridged complexes and $Na[N_3CS_2]$

A solution of 1 mmol of the $[(\pi\text{-allyl})PdCl]_2$ or $[(dieneOCH_3)MCl]_2$ in 10 ml of methanol was treated with a slight excess of the sodium salt of the azidodithiocarbonate. After few minuts the complex was obtained by addition of diethyl ether. Analytically pure samples were obtained by recrystallization from dichloromethane/*n*-hexane. Analytical data and physical properties of these complexes were identical with those obtained with the method described above.

Preparation of $[(\pi\text{-}C_3H_5)Pd(N_3SCNC_6H_5)]_2$ and $[(C_{10}H_{12}OCH_3)M(N_3SCNC_6H_5)]_2$ (M = Pd, Pt)

A solution of the appropriate azido complex (1.0 mmol) in dichloromethane (25 ml) was treated at 0° C with an excess of freshly distilled C_6H_5NCS dissolved in the same solvent. After 5 minutes the resulting pale yellow solution was treated with pentane giving a precipitate which was filtered and washed with ether. Crystallization from dichloromethane/*n*-hexane gave the complex in > 75% yield. This compound decomposes in solution but it can be stored for several days under nitrogen in the dark.

Decomposition of the 5-thio-1,2,3,4-thiatriazolato Complexes

The complexes of the type $[(\pi\text{-allyl})Pd(N_3CS_2)]_2$ and $[(dieneOCH_3)M(N_3CS_2)]_2$ decompose slowly in solution of $CHCl_3$, CCl_4, CS_2 to give brown polymeric species insoluble in organic solvents. In a typical decomposition experiment the complex $[(\pi\text{-}C_3H_5)Pd(N_3CS_2)]_2$ was dissolved in CS_2 and allowed to stand at 46° C until the disappearance of the characteristic i.r. absorptions of the thiatriazolato ring. During this period a brown precipitate was formed. Althought the i.r. spectrum of the decomposition product indicates the formation of thiocyanate bridged complex its analytical data and physical properties do not agree with those of a sample of $[(\pi\text{-}C_3H_5)PdNCS]_2$ prepared by metathetical exchange from $[(\pi\text{-}C_3H_5)PdCl]_2$ with KCNS.

Results and Discussion

The new azido-bridged complexes $[(\pi\text{-allyl})PdN_3]_2$ and $[(\text{dieneOCH}_3)MN_3]_2$ (M = Pd, Pt; π-allyl = $\pi\text{-}C_3H_5$, $\pi\text{-}C_6H_9$; diene = cycloocta-1,5-diene, cycloocta-1,3-diene, dicyclopentadiene and cyclooctatetraene) have been prepared by metathetical exchange

TABLE I. Colours, Decomposition Temperatures, Analytical and Molecular Weight Data for Pd(II) and Pt(II) Complexes.

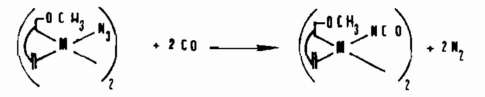
Compound	Colour	M.p. °C (dec.)	Analyses, % found (calcd.)					Mol Wt.[a] found (cald.)
			C	H	N	S	OCH$_3$	
$[(\pi\text{-}C_3H_5)PdN_3]_2$	Yellow	98–101	18.9 (19.01)	2.6 (2.66)	22.5 (22.18)	–	–	382 (379)
$[(\pi\text{-}1,3\text{-}C_6H_9)PdN_3]_2$	Yellow	99–102	32.2 (31.39)	3.8 (3.95)	18.1 (18.31)	–	–	–
$[(\pi\text{-}1,3\text{-}C_8H_{13})PdN_3]_2$	Yellow	134–137	37.8 (37.30)	4.4 (5.08)	16.1 (16.32)	–	–	–
$[(C_8H_8OCH_3)PdN_3]_2$	Pale Yellow	132–135	38.1 (38.11)	3.7 (3.91)	14.5 (14.82)	–	11.0 (10.94)	–
$[(1,3\text{-}C_8H_{12}OCH_3)PdN_3]_2$	Pale Yellow	116–120	37.7 (37.58)	5.5 (5.25)	14.8 (14.61)	–	11.1 (10.79)	–
$[(1,5\text{-}C_8H_{12}OCH_3)PdN_3]_2$	White	141–144	37.4 (37.58)	5.2 (5.25)	14.5 (14.61)	–	11.3 (10.79)	586 (575)
$[(C_{10}H_{12}OCH_3)PdN_3]_2$	Pale Yellow	186–188	42.5 (42.39)	4.8 (4.85)	13.4 (13.49)	–	10.1 (9.96)	627 (623)
$[(1,5\text{-}C_8H_{12}OCH_3)PtN_3]_2$	Pale Yellow	150–152	27.5 (28.72)	3.8 (4.02)	11.3 (11.17)	–	8.2 (8.25)	–
$[(C_{10}H_{12}OCH_3)PtN_3]_2$	White	178–182	32.9 (33.00)	3.7 (3.78)	10.5 (10.50)	–	7.7 (7.75)	795 (801)
$[(\pi\text{-}C_3H_5)PdNCO]_2$	Ivory	138–140	25.7 (25.35)	2.5 (2.66)	7.1 (7.39)	–	–	385 (379)
$[(C_{10}H_{12}OCH_3)PdNCO]_2$	Ivory	194–196	45.5 (46.24)	4.3 (4.85)	3.9 (4.49)	–	9.8 (9.96)	–
$[(C_{10}H_{12}OCH_3)PtNCO]_2$	White	209–211	36.3 (36.00)	3.6 (3.78)	3.1 (3.48)	–	7.8 (7.75)	787 (801)
$[(\pi\text{-}C_3H_5)PdNCS]_2$	White	177–179	23.5 (23.5)	2.5 (2.43)	6.7 (6.82)	–	–	401 (411)
$[(\pi\text{-}C_3H_5)Pd(N_3CF_3CN)]_2$	White	183–185	21.3 (21.25)	2.1 (1.78)	19.1 (19.70)	19.89[b] (20.17)	–	572 (569)
$[(\pi\text{-}C_3H_5)Pd(N_3CS_2)]_2$	Yellow	89–90	17.9 (18.08)	2.0 (1.89)	15.2 (15.82)	24.3 (24.14)	–	510 (532)
$[(1,3\text{-}C_8H_{12}OCH_3)Pd(N_3CS_2)]_2$	Yellow	95–96	32.8 (33.01)	4.2 (4.16)	10.8 (11.55)	17.9 (17.63)	–	–
$[(1,5\text{-}C_8H_{12}OCH_3)Pd(N_3CS_2)]_2$	Brown Yellow	96–98	32.7 (33.01)	4.1 (4.16)	11.4 (11.55)	18.0 (17.63)	–	705 (728)
$[(C_{10}H_{12}OCH_3)Pd(N_3CS_2)]_2$	Yellow	112–115	37.7 (37.16)	3.8 (3.90)	9.7 (10.84)	15.9 (16.53)	–	650 (776)
$[(C_{10}H_{12}OCH_3)Pt(N_3CS_2)]_2$	Yellow	102–105	30.8 (30.25)	3.3 (3.17)	8.4 (8.82)	13.8 (13.46)	–	930 (952)
$[(\pi\text{-}C_3H_5)Pd(N_3SCNC_6H_5)]_2$	Yellow	108–109	36.9 (36.99)	3.2 (3.10)	16.3 (17.26)	9.6 (9.87)	–	623 (649)
$[(C_{10}H_{12}OCH_3)Pd$ $(N_3SCNC_6H_5)]_2$	Pale Yellow	168–171	48.6 (48.38)	4.3 (4.51)	11.8 (12.54)	7.0 (7.17)	–	–
$[(C_{10}H_{12}OCH_3)Pt$ $(N_3SCNC_6H_5)]_2$	Yellow	195–197	41.0 (40.37)	3.4 (3.76)	8.9 (10.46)	5.03 (5.99)	–	–

[a] 1.2-dichloroacethane solution. [b] F analysis.

from the analogous chloro-bridged complexes. Analytical data and some physical properties for these complexes are reported in Table I. They are soluble in chlorinated solvents, insoluble in hydrocarbons, slightly soluble in alcohol. These complexes are stable in the solid state but they slowly decompose in solution. Molecular weight measurements in 1,2-dichloroethane solution show their dimeric nature. The i.r. spectra, reported in Table II, show that the positions of the $\nu_{as}(N_3)$ and $\nu_s(N_3)$ are practically unchanged by varying the coordinated olefin. The infrared asymmetric N_3 stretching of the azido complexes fall in the range 2050–2070 cm^{-1} and is the same in both solution and the solid state. This observation together with the data of molecular weight measurements are indicative for the dimeric nature of the azido complexes both in solid state and in solution. On the basis of our data alone it was not possible to establish the mode of coordination of the azido ligand, that is, whether it is of type A or of type B (*vide supra*).

Reaction of Azido Complexes with CO

It has been shown that monomeric azido complexes of the types $(CO)ML_2N_3$ (M = Rh, Ir) and $M(N_3)_2L_2$ (M = Pd, Pt) react with carbon monoxide to give the corresponding cyanato complexes[18,19,20]. A similar reaction occurs with $[(L_\pi)_2RhN_3]_2$ (L_π = CO, 1/2 (diolefin)) in which the N_3^- group is bridging two rhodium atoms[8]. In analogy with the rhodium complexes the azido derivatives of Pt(II) and Pd(II) here reported react with carbon monoxide to give the NCO-bridged complexes:

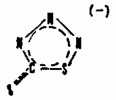


These compounds have been characterized by elemental analysis and molecular weight measurements (Table I). Their i.r. spectra show the $\nu_{as}(NCO)$ in the range 2165–2170 cm^{-1} and the $\nu_s(NCO)$ in the range 1290–1340 cm^{-1}; both position and intensity are in agreement with those of the same compounds prepared by metathesis from the corresponding Cl-bridged compounds and KCNO in acetone solution. The $\nu_{as}(NCO)$ band is shifted toward lower wavelength with respect to that of terminal NCO complexes of Pt(II) and Pd(II) indicating the bridging nature of the NCO ligand[21,22].

1,3-Dipolar Cycloaddition Reactions

Reaction with carbon disulfide

If the complexes of the type $[(\pi\text{-allyl})PdN_3]_2$ and $[(dieneOCH_3)MN_3]_2$ are treated with an excess of CS_2 in dichloromethane solution a rapid exothermic reaction occurs. The reactions can be followed by the disappearance of the asymmetric azide stretching band of the starting complexes and the appearance of new bands in the 1000–1300 cm^{-1} region that can be assigned to the five-membered heterocyclic anion formed by the 1,3-dipolar cycloaddition of the bridged azide to the CS_2 dipolarophile:



It is worth to point out that similar reactions have been found in terminal azido bridged complexes of Pt(II) and Pd(II)[23], Cu(I), Ag(I) and Au(I)[24] whereas the reactions here reported are the first example of 1,3-dipolar cycloaddition of the azido bridging group

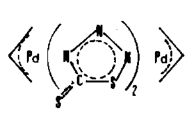
TABLE II. Infrared Data for N_3, NCO and NCS Bridged Complexes.

Compound	Stretching Bands (cm^{-1})[a]		
	$\nu_{as}(N_3)$	$\nu_s(N_3)$	$\nu(\text{–C–O–CH}_3)$
$[(\pi\text{-}C_3H_5)PdN_3]_2$	2055 s	1289 m–s	–
$[(\pi\text{-}1,3\text{-}C_6H_9)PdN_3]_2$	2050 s	1275 m–s	–
$[(\pi\text{-}1,3\text{-}C_9H_{13})PdN_3]_2$	2053 s	1283 m–s	–
$[(C_8H_8OCH_3)PdN_3]_2$	2050 s	1285 m	1102 s
$[(1,3\text{-}C_8H_{12}OCH_3)PdN_3]_2$	2055 s	1291 m	1094 s
$[(1,5\text{-}C_8H_{12}OCH_3)PdN_3]_2$	2054 s	1292 m	1088 s
$[(C_{10}H_{12}OCH_3)PdN_3]_2$	2052 s	1289 m	1093 s
$[(1,5\text{-}C_8H_{12}OCH_3)PdN_3]_2$	2069 s	1274 m	1089 s
$[(C_{10}H_{12}OCH_3)PtN_3]_2$	2070 s	1267 m	1090 s
$[(\pi\text{-}C_3H_5)PdNCO]_2$	2165 s[b]	1340 w–m[c]	–
$[(C_{10}H_{12}OCH_3)PdNCO]_2$	2170 s[b]	1302 m[c]	1093 s
$[(C_{10}H_{12}OCH_3)PtNCO]_2$	2169 s[b]	1290 w–m[c]	1092 s
$[(\pi\text{-}C_3H_5)PdNCS]_2$	2151 s[d]	779 w[e]	–

[a] Nujol Mull (± 5 cm^{-1}). [b] $\nu_{as}(NCO)$. [c] $\nu_s(NCO)$. [d] $\nu_{as}(NCS)$. [e] $\nu_s(NCS)$.

to CS_2. The carbon disulfide adducts have been isolated as crystalline material and characterized by elemental analyses and molecular weight measurements that indicate their dimeric nature in 1,2-dichloroethane solution. Their i.r. spectra show the presence of the coordinated 1,2,3,4-thiatriazole-5-thiolate group from its characteristic absorption bands[25] (Table III).

These evidences support a structure in which the thiatriazolate group is bridging two metal atoms:



The same complexes were also obtained from $[(\pi\text{-allyl})PdCl]_2$ or from $[(\text{dieneOCH}_3)MCl]_2$ and Na $[CS_2N_3]$ in methanol.

It is known that thiatriazolate complexes and organic substituted thiotriazoles decompose to give thiocyanate derivatives[23,24,26]. The decomposition of our $[(\pi\text{-allyl})Pd(N_3CS_2)]_2$ and $[(\text{dieneOCH}_3)M(N_3CS_2)]_2$ in $CHCl_3$ solution leads to a brown polymeric material insoluble in organic solvents. These decompositions may be followed by the disappearance of the characteristic i.r. absorption at ~ 1250 cm^{-1} of the thiocarbonyl group of the coordinated thiatriazole ring. The i.r. spectrum of the final product shows an intense band at 2150 cm^{-1} indicating an isothiocyanate complex. The unusually high infrared active CN stretching frequencies observed for these decomposition product indicate the presence of the NCS-bridging group[27]. Despite this i.r. evidence the analytical data and the physical properties of the decomposition product are not consistent with those of the corresponding isothiocyanate complexes prepared from the chloro-bridged derivatives and KCNS:

$$[(\pi\text{-}C_3H_5)PdCl_2]_2 + 2\,NCS^- \rightarrow [(\pi\text{-}C_3H_5PdNCS]_2 + 2\,Cl^-$$

Elemental analysis of the decomposition products indicate a M/S ratio = 1/2, moreover during the decomposition N_2 is liberated quantitatively, whereas no elemental sulfur is detected in the reaction products; if the decomposition reaction is carried out in presence of $P(C_6H_5)_3$ no $(C_6H_5)_3PS$ is recovered. These evidences, although not definitive, indicate that the decomposition of the CS_2 addition products leads to polymeric derivatives in which sulfur is probably bonded to the metal. The decomposition of the CS_2 adducts is at present under investigation.

Reaction with trifluoroacetonitrile

CF_3CN reacts in CH_2Cl_2 solution with $[(\pi\text{-}C_3H_5)PdN_3]_2$ to form perfluoromethyltetrazolate complexes, *via* 1,3-cycloaddition at the azide bridging moiety:

$$[(\pi\text{-}C_3H_5)PdN_3]_2 + 2\,CF_3CN \rightarrow [(\pi\text{-}C_3H_5)PdN_3CF_3CN]_2$$

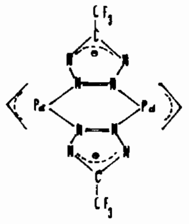
This reaction is slower than that with CS_2 and takes about 15 hr to go to completion. The azido complexes $[(\text{dieneOCH}_3)MN_3]_2$ also react with CF_3CN. In these cases the reactions are even slower and after 3 days the infrared spectra of the reaction mixture still show $\nu_{as}(N_3)$ at 2060 cm^{-1} in addition to the characteristic bands of the produced 5-trifluoromethyltetrazolate anion[28,29,30].

TABLE III. Infrared Data for Cycloaddition Products of the Azido Complexes.

Compound	Selected Bands[a]
$[(\pi\text{-}C_3H_5)Pd(N_3CS_2)]_2$	1320m, 1283m, 1256s (ν C=S), 1107s, 1057s (ν C–N), 906m (δ –N–S–C–)
$[(1,3\text{-}C_8H_{12}OCH_3)Pd(N_3CS_2)]_2$	1247s (ν C=S), 1108s (ν C–N), 1096sh (ν C–O–CH_3), 908m (δ –N–S–C–)
$[(1,5\text{-}C_8H_{12}OCH_3)Pd(N_3CS_2)]_2$	1245s (ν C=S), 1099sh, 1075sh (ν C–N), 1086s (ν C–O–CH_3), 912m (δ –N–S–C–)
$[(C_{10}H_{12}OCH_3)Pd(N_3CS_2)]_2$	1251s (ν C=S), 1101s, 1074s (ν C–N), 1090s (ν C–O–CH_3), 907m (δ –N–S–C–)
$[(C_{10}H_{12}OCH_3)Pt(N_3CS_2)]_2$	1255s (ν C=S), 1100s, 1075s (ν C–N), 1085s (ν C–O–CH_3), 909m (δ –N–S–C–)
$[(\pi\text{-}C_3H_5)Pd(N_3CF_3CN)]_2$	1512m (ν C–CF_3), 1249m, 1191s, 1171s, 1150s, 1146sh (ν CF_3), 1067m[b], 1026s[b], 753m (δ C–CF_3)
$[(1,5\text{-}C_8H_{12}OCH_3)Pd(N_3CF_3CN)]_2$	1504m (ν C–CF_3), 1250m, 1185s, 1170s, 1150s (ν CF_3), 1098s (ν C–O–CH_3), 1070m[b], 1025s[b], 754m (δ C–CF_3)
$[(1,5\text{-}C_8H_{12}OCH_3)Pt(N_3CF_3CN)]_2$	1510m (ν C–CF_3), 1248m, 1190s, 1170s, 1152s (ν CF_3), 1092s (ν C–O–CH_3), 1068m[b], 1026s[b], 752m (δ C–CF_3)
$[(\pi\text{-}C_3H_5)Pd(N_3C_6H_5NCS)]_2$	1550s, 1505s, 1318s, 1242m, 1198m, 1100s, 780m, 728m, 708s, 696m
$[(C_{10}H_{12}OCH_3)Pd(N_3C_6H_5NCS)]_2$	1525s, 1495m, 1315m, 1240m, 1200m, 1092sh, 1085s, 780m, 723m, 707s, 693m

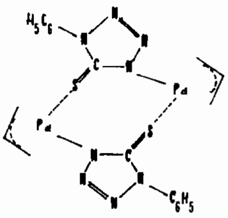
[a] Nujol Mull, cm^{-1}. [b] Heterocyclic ring vibrations.

The addition product $[(\pi\text{-}C_3H_5)PdN_3CNCF_3]_2$ is dimeric in 1,2-dichloroethane solution and the tetrazole ring probably behaves as a bidentate ligand as found for the complex $[Ag(P(C_6H_5)_3)(N_3CNCF_3)]_2$[24]:



Reaction with phenylisothiocyanate and carbonylsulfide

The azido complexes react with other dipolarophiles such as C_6H_5NCS and COS. In both cases a 1,3-cycloaddition to coordinated bridging N_3 group occurs. In the former case the final product analyses as $[(\pi\text{-}C_3H_5)Pd(N_3SCNC_6H_5)]_2$ and $[(dieneOCH_3)M(N_3SCNC_6H_5)]_2$ (M = Pt, Pd) and are dimeric in dichloromethane solution. The i.r. spectra shows bands near 1250 cm^{-1} attributable to the thiocarbonyl group of the 1-phenyltetrazolate-5-thione. It must be noted that the $\nu(C{=}S)$ of the uncoordinated 1-phenyltetrazoline-5-thione falls at 1361 cm^{-1}[31]. The lowering we observed could be attributed to a possible S-coordination of the thioketone group to the metal.



The reaction between $[(\pi\text{-}C_3H_5)PdN_3]_2$ and COS in CH_2Cl_2 solution does not lead to stable cycloaddition product, but to a brown, probably polymeric material, insoluble in all the common organic solvents. The i.r. spectrum of the final product shows a band at 2165 cm^{-1} that could be assigned to $\nu_{as}NCO$. The absence in the i.r. spectrum of $\nu_{as}N_3$ and of the bands due to the thiazolate ring (N_3COS) indicate that the cycloaddition product $[(\pi\text{-}C_3H_5)PdN_3COS]_2$ decomposes very rapidly to a cyanate derivative that is probably similar to the products obtained from the decomposition of the thiatriazolate derivatives.

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