Stereochemical Aspects of the Cycloaddition Reaction Products of the Coordinated Azide in Palladium Complexes [Pd(N–N–S)(N_3)]

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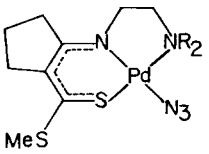
Abstract

Cycloaddition reactions of coordinated azide in the palladium(II) complexes [PdL(N_3)] (L = L^1–L^3; HL^1 = methyl 2-(2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate, HL^2 = methyl 2-((2-dimethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate, HL^3 = methyl 2-((2-diethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate)) with nitriles, alkynes, alkenes, PhNCS and CS_2 have been investigated. In all the cases the products obtained are of the type [PdL(heterocycle)$^-$]. The tetrazolates obtained by reacting [PdL(N_3)] with nitriles give rise to *syn*-N(1)-, *anti*-N(1)- and N(2)-bound isomers, whose relative abundances have been determined from ^{1}H NMR spectra. The relative abundance of the N(2)-bound species increases with electron-withdrawing substituents on the tetrazolates. The triazolato and triazolinato complexes obtained from alkynes and alkenes, repectively exist only as the N(2) isomer. The rate constants for the reaction of [PdL(N_3)] with aromatic nitriles show a strong dependence on σ_p (Hammett parameters) of the substituent. The reaction rate also depends upon the steric influences of the substituents attached to the terminal nitrogen atom of L and decreases in the order: [$PdL^1(N_3)$] > [$PdL^2(N_3)$] > [$PdL^3(N_3)$].

Introduction

1,3-Dipolar cycloadditions of multiple bonded molecules to coordinated azide in metal complexes have emerged as a simple but powerful method for generating various (many of which are otherwise inaccessible) metal bound heterocycles [1–9]. The stereochemical aspects of these cycloaddition products are of considerable interest because the polynitrogen heterocycles thus produced are ambidentate ligands that may bind to the metal center via different donor atoms. Moreover, peripheral substituents in a complex molecule may restrict rotation of the heterocyclic ring and lead to occurrence of conformational equilibria. Electronic and steric factors, therefore, are expected to play dominant roles in determining the relative abundances of linkage isomers and conformers, as well as on the kinetics of the cycloaddition reactions. The present study which deals with the reactions of nitriles, alkynes, alkenes, PhNCS and CS_2 with coordinated azide in palladium(II) chelates of the type [PdL(N_3)] (**1a**–**1c**) aims to investigate all these aspects.



1a: [$PdL^1(N_3)$], R = H
1b: [$PdL^2(N_3)$], R = Me

Experimental

Materials

All chemicals were reagent grade and were used without further purification. The ligands [10] methyl 2-((2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate (HL^1), methyl 2-((2-(dimethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate (HL^2) and methyl 2-((2-diethylamino)ethyl)amino)cyclopent-1-enedithiocarboxylate (HL^3) and their palladium(II) complexes [PdL(NCMe)](ClO_4) [11] were prepared as described earlier. *p*-$NO_2C_6H_4CN$ and *p*-ClC_6H_4CN were prepared from the corresponding aldehydes [12] and PhCOC≡CCOPh was obtained according to a known method [13].

Synthesis of the Complexes

Azido complexes

[PdL(N_3)] (L = L^1–L^3, 1a–1c). To a MeCN solution (30 cm^3) of [PdL(MeCN)](ClO_4) (5 mmol) an aqueous solution (5 cm^3) of NaN_3 (0.33 g, 5 mmol)

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was slowly added with stirring. After additional stirring for 1 h, the yellow product was collected by filtration, washed successively with water, MeCN and MeOH, and recrystallized from Me_2CO. Typical yields were >90%.

Tetrazolate complexes

[$PdL^1(N_4C–R)$] (R = Me (2), Et (3)). [$PdL^1(N_3)$] (0.5 g) was mixed with MeCN (50 cm^3) or EtCN (30 cm^3) and heated under reflux for 12 h. The solution was concentrated on a rotary evaporator to *c.* 10 cm^3 and filtered. The filtrate on standing overnight afforded yellow crystals which were recrystallized from Me_2CO (80%).

[$PdL^1(N_4C–Ph)$] (4). A mixture of [$PdL^1(N_3)$] (0.5 g) and PhCN (25 cm^3) was heated on a steam-bath for 2 h and then filtered hot. The filtrate was again heated for 6 h during which deep yellow crystal deposited. The product was collected by filtration, washed with MeOH and recrystallized from $MeNO_2$ (70%).

[$PdL^1(N_4C$-p-$ClC_6H_4)$] (5), [$PdL^1(N_4C$-p-$NO_2C_6H_4)$] (6). [$PdL^1(N_3)$] (0.36 g, 1 mmol) was dissolved in hot $PhNO_2$ (10 cm^3) and *p*-ClC_6H_4CN or *p*-$NO_2C_6H_4CN$) (4 mmol) was added. On heating the solution at *c.* 100 °C for 4 h yellow–green crystals deposited, which were collected by filtration and recrystallized from hot (100 °C) *N,N*-dimethylformamide (80%).

[$PdL(N_4(C$-R)] (L = L^2: R = Me (7), Et (8), Ph (9); L = L^3: R = Me (10), Et (11), Ph (12)). A solution of [$PdL(N_3)$] (1 mmol) in MeCN (30 cm^3), EtCN (20 cm^3) or PhCN (10 cm^3) was heated on a steam-bath for 15 h, following which it was filtered and concentrated (5 cm^3) on a rotary evaporator. The product which deposited on cooling the solution in a refrigerator overnight was collected by filtration, washed with MeOH and recrystallized from 1:1 $CHCl_2$–Et_2O (70–75%).

[$PdL^3(N_4C$-p-$NO_2C_6H_4)$] (13). To a boiling CH_2Cl_2 solution (50 cm^3) or [$PdL^3(N_3)$] (0.42 g, 1 mmol) *p*-$NO_2C_6H_4CN$ (0.6 g, 4 mmol) was added and refluxing was continued for 5 h. The product obtained as light yellow crystals was recrystallized from CH_2Cl_2 (80%).

Triazolato complexes

[$PdL(N_3C_2R_2$)] (L = L^1: R = CO_2Me (14), COPh (15); L = L^2: R = CO_2Me (16), COPh (17); L = L^3: R = CO_2Me (18), COPh (19)). A mixture containing [$PdL(N_3)$] (1 mmol), CH_2Cl_2 (30 cm^3) and MeO_2C–C≡C–CO_2Me (0.5 cm^3) or Ph(CO)C≡C(CO)Ph (0.5 g) was heated under reflux for 2 h. The product was isolated by concentrating the solution and recrystallized either from CH_2Cl_2 (**14**, **15**) or from 1:1 CH_2Cl_2–Et_2O (**16**–**19**) (70–75%).

Triazolinato complexes

[$PdL^1\{N_3C_2H_2(CO_2Me)_2\}$] (20). A $PhNO_2$ (5 cm^3) solution containing [PdL^1N_3] (0.42 g, 1 mmol) and dimethylfumarate (0.58 g, 4 mmol) was heated at 100 °C for 4 h. The red–brown crystals that deposited from the solution were isolated by filtration and recrystallized from Me_2CO (50%).

[$PdL^1\{N_3C_2H_3(CN)\}$] (21). A solution containing acrylonitrile (5 cm^3) and [$PdL^1(N_3)$] (0.5 g) in Me_2CO (30 cm^3) was heated at reflux under a N_2 atmosphere for 10 h. The orange–yellow crystals obtained by slow evaporation of the solvent were recrystallized from Me_2CO (50%).

Tetrazolinthionato complexes

[PdL($N_4C(S)Ph$)] (L = L^1 (22), L^2 (23)). To a boiling Me_2CO solution (50 cm^3) of the azido complex (0.5 g) PhNCS (4 cm^3) was added in small portions. After 5 h reflux the product was isolated by partial removal of the solvent. Complex **22** was recrystallized from CH_2Cl_2 and **23** from 1:1 CH_2Cl_2–Et_2O (*c.* 70%).

Thiothiazolinato complex

[$PdL^1(N_3C(S)S$)] (24). A suspension of [$PdL^1(N_3)$] (0.5 g) in CS_2 (30 cm^3) was stirred for 16 h at 20 °C, during which the original yellow color became brown. The product was collected on a glass frit and washed freely with Me_2CO (to remove any unreacted azido complex) and $CHCl_3$ (to remove [$PdL^1(NCS)$] formed). The product (80%) was insoluble in a variety of solvents and could not be recrystallized due to the lack of a suitable solvent.

Analytical data for selected compounds are given in Table 1.

Physical Measurements

^1H NMR spectra were recorded on $CDCl_3$ or Me_2SO-d_6 solutions on either a Bruker 270 MHz or Varian 100 MHz spectrometers using Me_4Si (δ = 0 ppm) as the internal reference. IR spectra were carried out as KBr pellets using a Perkin-Elmer Model 783 infrared spectrophotometer and electronic spectra were recorded using a Pye-Unicam SP8-150 spectrophotometer. C, H, and N analyses were performed on a Perkin-Elmer Model 240C elemental analyzer. Palladium was estimated gravimetrically as the dimethylglyoximate.

TABLE 1. Analytical data for some palladium(II) complexes

Compound	Found (%)				Calculated (%)			
	C	H	N	Pd	C	H	N	Pd
1a	30.02	4.28	18.98	29.09	29.74	4.13	19.26	29.28
2	32.48	4.56	20.65	26.23	32.64	4.45	20.74	26.31
3	34.24	4.67	20.27	25.56	34.42	4.78	20.08	25.43
4	41.0	4.19	18.24	23.01	41.17	4.29	18.01	22.81
5	38.51	3.68	16.61	21.35	38.33	3.79	16.74	21.24
6	37.21	3.65	18.98	20.72	37.54	3.71	19.16	20.80
7	36.25	5.21	19.62	24.65	36.08	5.09	19.43	24.61
8	37.74	5.55	18.71	24.03	37.63	5.38	18.82	23.83
10	38.78	5.72	18.05	23.01	39.10	5.65	18.24	23.11
12	46.19	5.45	16.30	20.24	45.94	5.36	16.08	20.37
13	42.52	4.87	17.45	18.63	42.30	4.76	17.27	18.75
14	35.93	4.26	14.03	21.0	35.61	4.15	13.85	21.05
15	50.35	4.27	11.81	17.92	50.21	4.18	11.72	17.81
17	51.60	4.51	11.12	16.88	51.81	4.64	11.13	17.01
20	35.25	4.56	13.86	20.84	35.40	4.72	13.77	20.93
22	38.21	3.85	16.57	21.49	38.52	4.01	16.85	21.35
24	27.02	3.25	15.66	24.36	27.31	3.41	15.93	24.21

Kinetic Measurements

The reaction kinetics were followed spectrophotometrically in an IR spectrophotometer between 60 and 80 °C (±0.2 °C). All reactions were investigated under pseudo-first-order conditions with 5×10^{-3} mol dm^{-3} of each azido complex and 0.5 mol dm^{-3} nitriles in nitrobenzene. Small aliquots of thermally equilibriated reaction mixtures were periodically quench-cooled and the change in transmittance due to $\nu_{as}[N_3^-]$ in the range 2100–2000 cm^{-1} was monitored in a NaCl cell against a matched cell containing the solvent as blank. Preliminary experiments established that the transmittance of the azide vibration is proportional to the concentration of azide.

Results and Discussion

Aliphatic and aromatic nitriles readily react with the azido complexes **1a–1c** to produce tetrazolate complexes **2–13**. The formation of tetrazolate complexes can be followed by observing the disappearance of $\nu_{as}[N_3]$ (*c.* 2040 cm^{-1}) and $\nu_s[N_3]$ (*c.* 1340 cm^{-1}) and the appearance of new bands due to tetrazole ring vibrations [14–17] in the range 1250–750 cm^{-1} (Table 2).

1,3-Dipolar cycloaddition of nitriles to the azido complexes can lead to the formation of either N(1)- or N(2)-bound tetrazole. Energetically, these two binding modes do not differ significantly [18–20]; as a result, simultaneous formation of both isomers can take place. However, molecular models indicate that while the N(2)-bound tetrazole is free to rotate, similar rotation of the N(1) isomer may be restricted due to steric interactions between the peripherial substituents of both the principal ligand (L) and tetrazole. Accordingly, a dynamic equilibrium may be established in solution between *syn*- and *anti*-conformers of the N(1)-bound tetrazole as illustrated in Scheme 1.

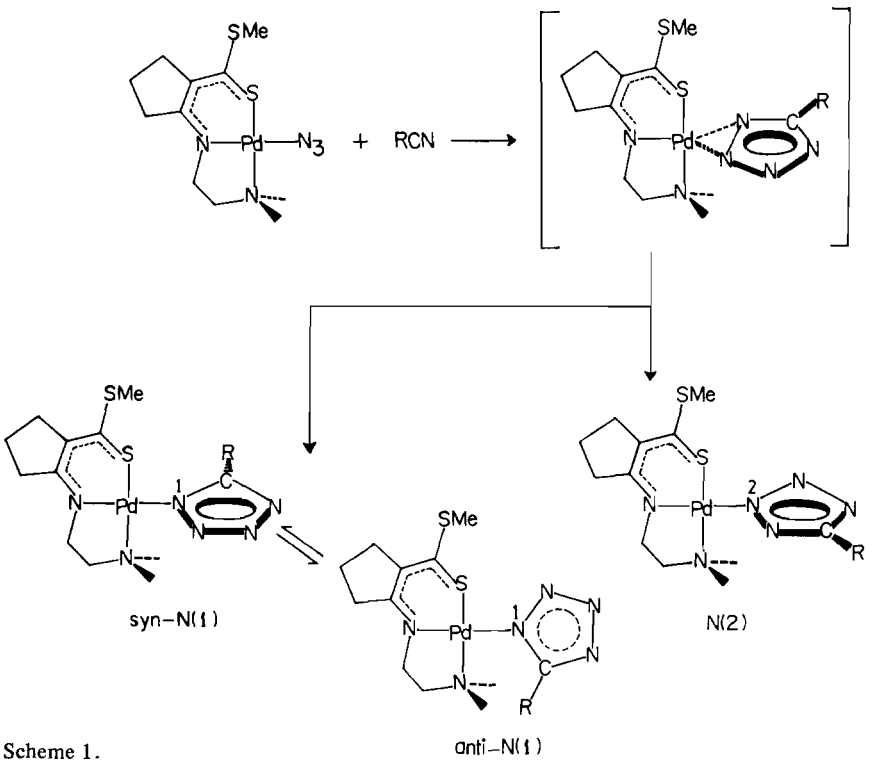
^1H NMR spectra of the cycloaddition products (Table 3) turned out to be extremely useful in characterizing all these isomers. The chemical shift for a substituent in the tetrazole moiety of an isomer is affected by its proximity to the metal center. The group closer to the metal is more deshielded due to the paramagnetic influence of the metal ion. A consideration of the steric disposition of R in tetrazolate (Scheme 1) reveals that while in N(2)-bound isomer R is furthest from the metal centre, it is closest in *anti* conformation of N(1)-bound tetrazolate. Thus, when *anti*-N(1)-, *syn*-N(1) and N(2)-bound species all coexist in solution the decreased order for shielding of the substituent R in a tetrazole is: *anti*-N(1)- > *syn*-N(1)- > N(2)-bound tetrazole.

The ^1H NMR spectrum of complex **2** (Fig. 1) exhibits three singlets at δ 2.31, 2.51 and 2.58 due to the CH_3 group of methyltetrazole and can be attributed to N(2)-, *syn*-N(1)- and *anti*-N(1)-bound tetrazole, respectively. Another singlet observed at $\delta = 2.48$ in this compound is due to the SCH_3 group of L^1. The two broad signals at δ 5.2 and 5.4 due to the NH_2 group of L^1 arise from a combination of the N(2) and *syn*-N(1) isomers, and the *anti*-N(1) isomer, respectively. The relative abundance of these three isomers was determined by measuring the intensities of all the CH_3 singlets as well as the NH_2 signals.

TABLE 2. Selected IR data (cm^{-1}) for some palladium(II) complexes[a]

1a	3250m, 3210m, 3130w (ν(NH)); 2040s ($\nu_{as}[N_3]$); 1340s ($\nu_s[N_3]$)
1b	2040s ($\nu_{as}[N_3]$); 1340s ($\nu_s[N_3]$)
1c	2040s ($\nu_{as}[N_3]$); 1340s ($\nu_s[N_3]$)
2	3210m, 3100m (ν(NH)); 1225m, 1160m, 1140m (tetrazole ring)
3	3230m, 3120m (ν(NH)); 1235m, 1155m, 1125m, 1075w (tetrazole ring)
4	3310m, 3200m; 3110m (ν(NH)); 1175w, 1075m, 1040m, 790m (tetrazole ring)
6	3310m, 3230m, 3130w (ν(NH)); 1175w, 1100m, 1040m, 780m (tetrazole ring)
10	1225m, 1085m, 1020m (tetrazole ring)
11	1155m, 1085m, 1030m (tetrazole ring)
12	1175m, 1070m, 1040m (tetrazole ring)
13	1175m, 1110m, 1040m (tetrazole ring)
14	3290m, 3190m, 3100m (ν(NH)); 1745s, 1725s (ν(CO)); 830m, 800m, 780m (triazole ring)
15	3300m, 3230m, 3130m (ν(NH)); 1660s, 1645s (ν(CO)); 900s, 810m, 760m (triazole ring)
18	1740s, 1720s (ν(CO)); 830m, 800m, 775m (triazole ring)
19	1660s, 1645s (ν(CO)); 900s, 825m, 810m, 760m (triazole ring)
20	3290m, 3200m, 3110m (ν(NH)); 1745s, 1725s (ν(CO)); 830m, 805m, 780m (triazoline ring)
21	3240m, 3200m, 3130m (ν(NH)); 2130m (ν(CN)); 810m, 780m (triazoline ring)
22	3310m, 3220m, 3110m (ν(NH)); 1155m, 1125m, 1090s, 1040m (tetrazolinethionate ring)
23	1170m, 1125w, 1090s, 1075s (tetrazolinethionate ring)
24	3270m, 3220m, 3130m (ν(NH)); 1140m, 1085s, 1030w, 1020m (thiothiazolinate ring)

[a]KBr pellets.

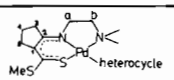


Scheme 1.

Measurements carried out in the temperature range 20–100 °C indicate that while the relative abundance of *syn* and *anti* conformers varies with temperature, the ratio between (*syn* + *anti*)-N(1)- and N(2)-bound methyltetrazole remains unchanged (2.4:1) throughout the entire temperature range. The equilibrium constant for *syn*-N(1) > *anti*-N(1) species (K = [*anti*]/[*syn*]) was found to vary with temperature in the following way: 0.74 (20 °C), 0.87 (40 °C), 1.02 (60 °C), 1.2 (80 °C) and 1.4 (100 °C). Thus, for

TABLE 3. ^{1}H NMR spectral data for the cycloaddition reaction products

Complex	Heterocyclic ring	Chemical shifts (δ)		Comment
		Principal ligand (L)	Heterocycle	
2[a]		L^1: 1.86m(4-CH_2); 2.48s(SCH_3); [2.6–2.9m] (3,5-CH_2 + b-CH_2); 3.66t(a-CH_2); [5.2 br, 5.4 br] (NH_2).	2.31s(CH_3, N(2)); 2.51s(CH_3, *syn*-N(1)); 2.58s(CH_3, *anti*-N(1)).	N(1):N(2) = 2.4:1; *syn*-N(1):*anti*-N(1) = 4:3 (at 20 °C)
7[b]		L^2: 1.98 m(4-CH_2); 2.54s(SCH_3); [2.61s, 2.67s] ($N(CH_3)_2$); [2.6–2.95m] (3,5-CH_2 + b-CH_2); 3.86t (a-CH_2).	2.52s(CH_3, N(2)); 2.53s(CH_3, *syn*-N(1)); 2.58s(CH_3, *anti*-N(1)).	
10[b]		L^3: [1.31t, 1.34t] ($N(CH_2$-$CH_3)_2$); 1.98m (4-CH_2); 2.70s(SCH_3); [2.5–3.2m] (3,5-CH_2 + b-CH_2 + $N(CH_2$-$CH_3)_2$); 3.82t (a-CH_2).	2.52s(CH_3, N(2)); 2.55s(CH_3, *syn*-N(1)); 2.59s(CH_3, *anti*-N(1))	
3[a]		L^1: 1.88m(4-CH_2); 2.48s(SCH_3); [2.5–3.1m] (3,5-CH_2 + b-CH_2 + N(2)-α-CH_2]; 3.68t (a-CH_2); [5.15 br, 5.4 br] (NH_2).	1.22t(N(2)-β-CH_3); 1.32t(N(1)-β-CH_3)N; 2.96q(N(1)-α-CH_2).	N(1):N(2) = 2:1
8[a]		L^2: 1.98m(4-CH_2); 2.56s(SCH_3); [2.56s, 2.59s] ($N(CH_3)_2$); [2.6–3.0m](3,5-CH_2 + b-CH_2 + N(2)-α-CH_2); 3.84m(a-CH_2).	1.37t(N(2)-β-CH_3); 1.46t(N(1)-β-CH_3); 3.13q(N(1)-α-CH_2).	N(1):N(2) = 3:2
4[a]		L^1: 1.89m(4-CH_2); 2.60s(SCH_3); [2.6–2.9m] (3,5-CH_2 + b-CH_2); 3.72t(a-CH_2); [5.15 br, 5.5 br] (NH_2).	7.5m(N(2)-C_6H_5); 8.1m (*syn*-N(1)-C_6H_5); 8.5m (*anti*-N(1)-C_6H_5)	N(1):N(2) = 2:3 *syn*-N(1):*anti*-N(1) = 8:1 (at 25 °C).
5[a]		L^1: 1.88m(4-CH_2); 2.56s(SCH_3); [2.6–2.9m] (3,5-CH_2 + b-CH_2); 3.70t(a-CH_2); [5.2 br, 5.5 br] (NH_2).	7.52d(N(1)-, N(2)-m-phenyl); 8.0d (*syn*-N(1)-*o*-phenyl); 8.48d(N(2)-*o*-phenyl)).	N(1):N(2) = 2:9
6[a]		L^1: 1.89m(4-CH_2); 2.61s(SCH_3); [2.6–2.9m] (3,5-CH_2 + b-CH_2); 3.75t(a-CH_2); 5.5 br (NH_2).	8.36m (phenyl)	N(2)-isomer
14[b]		L^1: 1.88m(4-CH_2); 2.56s(SCH_3); [2.6–2.8m] (3,5-CH_2); 3.14m(b-CH_2); 3.84t(a-CH_2); 5.1 br (NH_2).	3.86s(CO_2CH_3)	N(2)-isomer
15[b]		L^1: 1.88m(4-CH_2); 2.64s(SCH_3); [2.4–2.8m] (3,5-CH_2); 2.96 (b-CH_2); 3.78t(a-CH_2); 5.0 br (NH_2).	7.38m(*m*-, *p*-phenyl); 7.92m(*o*-phenyl).	N(2)-isomer
22[a]		L^1: 1.85m(4-CH_2); 2.52s(SCH_3); [2.5–2.9m] (3,5-CH_2 + b-CH_2); 3.68t (a-CH_2); 5.25 br (NH_2).	7.7m (phenyl)	N(2)-isomer

[a] In Me_2SO-d^6. [b] In $CDCl_3$. 

an increase of temperature by 80 °C a two-fold increase in the concentration of the *anti* conformer takes place over the *syn* conformer. A good linear fit was obtained for ln K versus $1/T$, wich gave ΔH = 1.7 Kcal mol^{-1} and ΔS = 5.2 cal mol^{-1} K^{-1}.

Similar to **2**, three isomeric species were expected for complex **3**. However, the ^{1}H NMR spectrum of this compound shows the presence of only two triplets (δ 1.22 and 1.32) due to the CH_3 group of ethyltetrazole. The NH_2 group of L^1 also appears as two broad signals at δ 5.15 and 5.40. The result indicates that for complex **3** only *syn*-N(1)- and N(2)-bound tetrazolates are present in solution and the relative abundance of N(1)- to N(2)-bound species is 2:1.

The ^{1}H NMR spectrum of complex **7** (Fig. 2) exhibits six singlets at δ 2.52, 2.53, 2.54, 2.58, 2.61

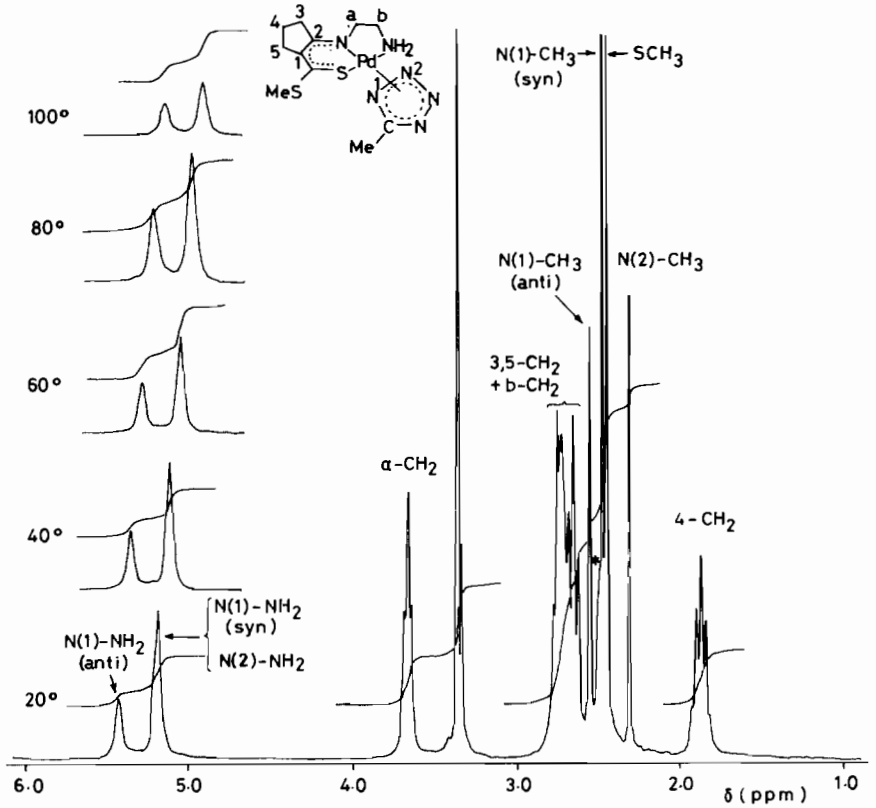


Fig. 1. ^{1}H NMR spectrum of [PdL^1(N$_4$C-Me)] (**2**) in Me_2SO-d_6. The signal marked (*) is due to the solvent.

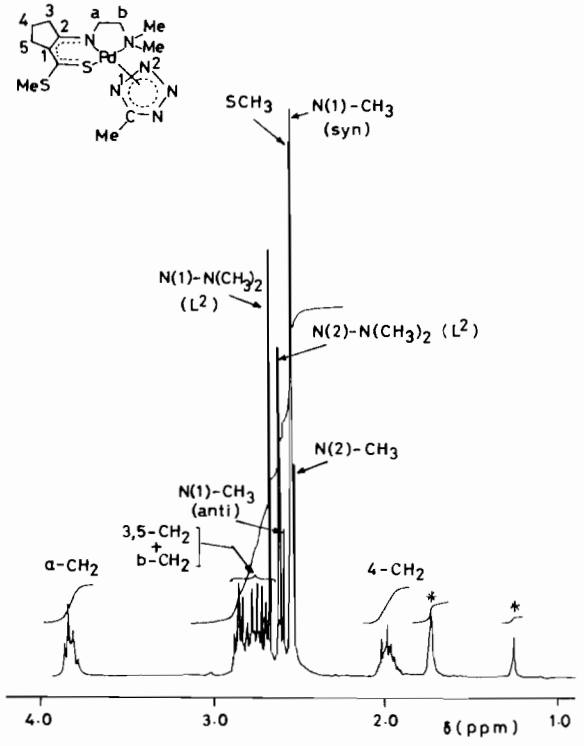


Fig. 2. ^{1}H NMR spectrum of [PdL^2(N$_4$C-Me)] (7) in $CDCl_3$. The signal marked (*) is due to the solvent.

and 2.67, of which the one at 2.54 is due to the SCH_3 group of L^2. The two most deshielded singlets (δ 2.67, 2.61) are attributed to the $N(CH_3)_2$ moiety of L^2 in the N(1) and N(2) isomers. The remaining three singlets at δ 2.52, 2.53 and 2.58 are due to the CH_3 group of 5-methyltetrazole in the N(2)-, *syn*-N(1)- and *anti*-N(1)-bound species, respectively. Because of strong overlapping effects of these resonances no estimate could be made of the relative abundance of the isomers in **7**.

The ^{1}H NMR spectrum for complex **10** (Fig. 3) again shows the presence of three isomers. Thus, aside from the singlet due to the SCH_3 group of L^3 (δ = 2.70), the three singlets due to 5-methyltetrazole at δ 2.52, 2.55 and 2.59 are attributable to the N(2)-, *syn*-N(1)- and *anti*-N(1)-bound species, respectively.

A consideration of molecular models for complex **8** indicated that the terminal $N(CH_3)_2$ moiety of L^2 imposes severe steric constraints on the *anti*-N(1)-bound 5-ethyltetrazole. The stereochemical aspect of this compound indeed is consistent with its ^{1}H NMR spectral features (shown in Fig. 4). The two triplets at δ 1.37 and 1.46 are due to the CH_3 group of 5-ethyltetrazole in the N(1) and N(2) isomers, and the two singlets at δ 2.56 and 2.59 are due to the $N(CH_3)_2$ group of L^2 in the two linkage isomers. The ratio of these two isomeric species was found to be 3:2.

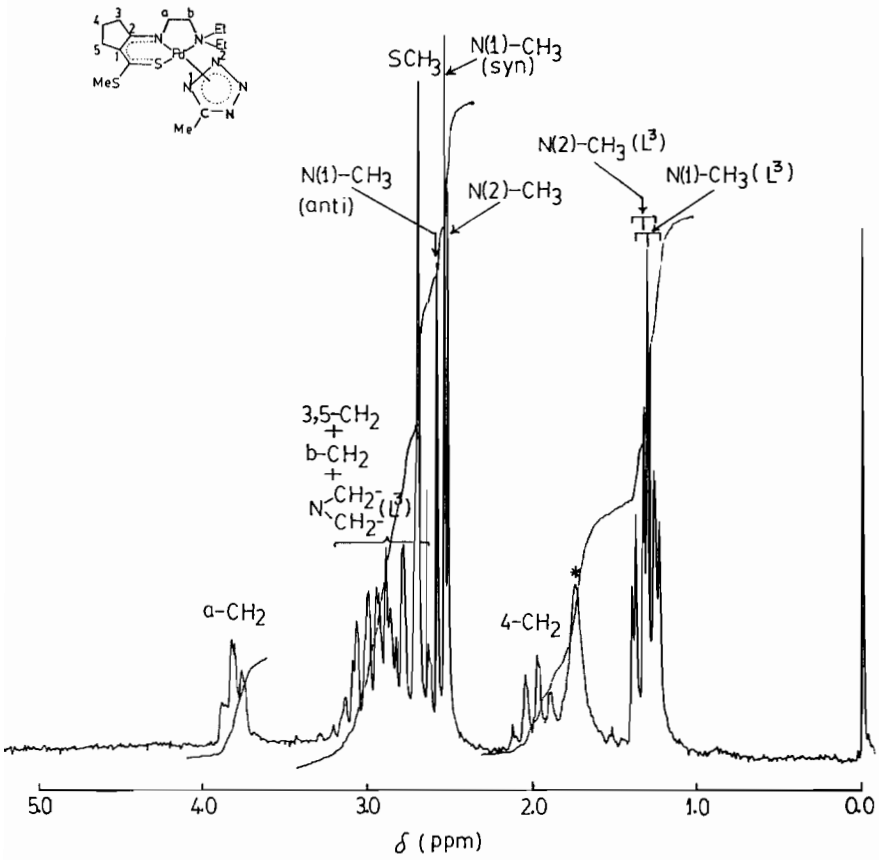


Fig. 3. ^{1}H NMR spectrum of [PdL^3(N$_4$C-Me)] (**10**) in $CDCl_3$. The signal marked (*) is due to the solvent.

In complex **4**, the phenyl substituent of the tetrazole exhibits three multiplets at *c.* 7.5, 8.1 and 8.5 having the intensity ratio 13.5:8:1, and the NH_2 protons of L^1 are observed at *c.* δ 5.15 and 5.5. It should be noted that the rotation of phenyltetrazole about the Pd–N(1) bond is quite restricted and this leads to a greater relative abundance of the *syn*-N(1) species over the *anti*-N(1) species (8:1). The overall ratio between the N(1)- and N(2)-bound isomers (3:2) is noteworthy; the relative abundance of the N(2) isomer has increased on replacing strongly electron-releasing alkyl substituents of tetrazole by the phenyl group. This effect becomes more pronounced for complex **5** bearing *p*-chlorophenyltetrazole. In this case the ratio of the N(1)- to N(2)-bound species is almost 2:9. The effect of the electron-withdrawing group can so destabilize the N(1)-bound tetrazole that with the *p*-nitrophenyl substituent complex **6** exists exclusively as the N(2)-bound species.

On the basis of these observations we suggest that the 1,3-dipolar cycloaddition reaction between [PdL(N$_3$)] complex and nitrile (RCN) takes place through the formation of a three-centered activated complex [21] (Scheme 1). The breaking of Pd–N(1) or Pd–N(2) bonds in the activated complex is governed by the electronic influence of the substituent R, but not temperature. It should be noted that with an electron-withdrawing R, preferential breakdown of the Pd–N(1) bond will take place because this nitrogen is electron-poor. On the other hand, when R is electron-releasing, the situation is reversed producing the N(1)-bound tetrazolate as the predominant species.

The rate constants obtained under pseudo-first-order conditions for the cycloaddition reactions of [PdL(N$_3$)] (L = L^1–L^3) complexes with aromatic nitriles (PhCN, *p*-ClC$_6$H$_4$CN, *p*-NO$_2$C$_6$H$_4$CN) are given in Table 4. The results show a strong dependence of the observed rate (k_{obs}) on the polarizing abilities of the dipolarophiles. Indeed, good linear fits were obtained from log k_{obs} versus σ_p (Hammett constants for the *p*-substituents). The order of reactivity of the nitriles, *p*-NO$_2$C$_6$H$_4$CN > *p*-ClC$_6$H$_4$CN > PhCN, parallels the decreasing electron-withdrawing power of the substituents in the same order.

The steric influences of the terminal N-substituents in the principal ligand (L) seem to play a domineering role in affecting the reaction rates. Thus, the reactivities of the [PdL(N$_3$)] complexes toward *p*-NO$_2$C$_6$H$_4$-

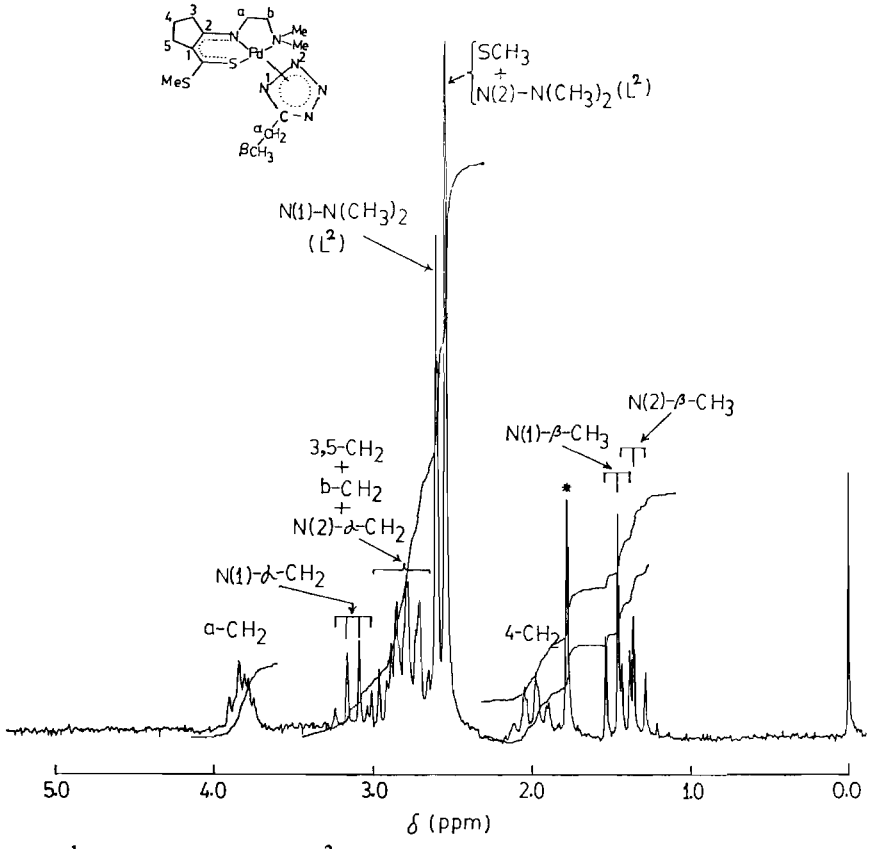


Fig. 4. ^{1}H NMR spectrum of [PdL^2(N$_4$C-Et)] (8) in $CDCl_3$. The signal marked (*) is due to the solvent.

TABLE 4. Rate constants for the cycloaddition reactions of azido complexes with nitriles

Complex	Dipolarophile	T (K)	$10^4 \times k_{obs}$ (s^{-1})	$10^2 \times k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)
[PdL^1(N$_3$)]	p-$NO_2C_6H_4CN$	353	10.54	21.1
		343	5.46	10.9
		333	2.36	4.72
	p-ClC_6H_4CN	353	1.19	2.38
	C_6H_5CN	353	0.22	0.55
[PdL^2(N$_3$)]	p-$NO_2C_6H_4CN$	353	5.61	1.12
[PdL^3(N$_3$)]	p-$NO_2C_6H_4CN$	353	1.32	0.26

CN which decrease in the order, [PdL^1(N$_3$)] > [PdL^2(N$_3$)] > [PdL^3(N$_3$)], can be related to the increasing steric encumbrance of L in the order, L^1 < L^2 < L^3.

Cycloaddition reactions are generally considered to take place in a concerted way [22] and involve a large negative entropy of activation ($\Delta S^{\neq}$) and a moderate enthalpy of activation ($\Delta H^{\neq}$). We note that the $\Delta H^{\neq}$ (15.8 kcal mol^{-1}) and $\Delta S^{\neq}$ (−17.2 cal $mol^{-1}\ K^{-1}$) values obtained for the reaction of [PdL^1(N$_3$)] with p-$NO_2C_6H_4CN$ support a concerted reaction mechanism.

Addition of alkynes to coordinated azide produces triazolates. Thus, dimethyl acetylenedicarboxylate and dibenzoylacetylene react with [PdL(N$_3$)] complexes to produce the triazolato complexes **14**–**19**. The IR spectra of these compounds (Table 2) show characteristic bands due to ν(C=O) (1745–1720 cm^{-1} for the CO_2Me groups and 1665–1625 cm^{-1} for the COPh groups) and triazole ring vibrations (900–700 cm^{-1}). Preliminary kinetic measurements indicated that both the alkyne derivatives react at faster rates than all the nitriles investigated. A detailed kinetic study, however, could not be carried out by IR spectrophotometric method because of the overlapping influence of ν(C≡C) on ν_{as}[N$_3$]. The ^{1}H NMR spectrum of complex **14** (Table 3) shows a singlet at δ = 3.86 due to the six carboxymethyl

protons. This is clearly indicative of the formation of only N(2)-bound triazolate because for the N(1) isomer two such singlets are expected for the anisochronous CO_2Me groups. The ^1H NMR spectrum of complex **15** also indicates the formation of the N(2) isomer as the sole product.

Alkenes such as dimethyl fumarate and acrylonitrile react with $[PdL^1(N_3)]$ to produce triazolinato complexes **20** and **21**, respectively. The IR spectrum of **20** is quite similar to that of **14** and the ^1H NMR spectrum of **20** (Table 3) also shows the formation of only N(2)-bound triazoline. It is interesting to note that although the addition of an alkyne or alkene to coordinated azide is expected to produce the N(1)-bound species, the N(2) linkage isomer is actually obtained. However, if the electronic and steric influences of the dipolarophiles are taken into consideration spontaneous conversion of the N(1) to N(2) isomer appears quite reasonable.

The azido complexes **1a** and **1c** react with PhNCS to produce stable tetrazolinthionato complexes **22** and **23**, respectively. These compounds exhibit multiple bands in the range 1170–1050 cm^{-1}, characteristic of terazolinthione ring vibrations. The ^1H NMR spectrum of **22** (Table 3) again shows the presence of a single isomer, presumably the N(2)-bound species.

Carbon disulfide undergoes a [3 + 2] cycloaddition reaction with the azido complexes at room temperature to give thiothiazolinato complexes, $[PdLN_3C(S)S]$. However, these are thermally unstable and decompose at temperatures above 40 °C to produce the corresponding isothiocyanato complexes , [PdL(NCS)].

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