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Bis(η^5-cyclopentadienyl)titanium Complexes Containing Sulfur Diimido and Thiazato Ligands. Crystal and Molecular Structure of (η^5-C_5H_5)$_2$Ti(NSO)$_2$

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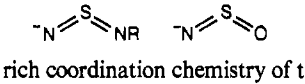
The reaction of (η^5-C_5H_5)$_2$TiCl$_2$ with K[NSN-*t*-Bu] yields the sulfur diimido complexes (η^5-C_5H_5)$_2$TiCl(NSN-*t*-Bu) (**1**) and (η^5-C_5H_5)$_2$Ti(NSN-*t*-Bu)$_2$ (**2**) depending upon the molar ratio of the reactants. Complex **2** undergoes hydrolysis on silica to give the dithiazato complex (η^5-C_5H_5)$_2$Ti(NSO)$_2$ (**5**). Compound **5** crystallizes in the orthorhombic space group *Fdd*2 with a = 29.219 (5) Å, b = 14.153 (3) Å, c = 6.189 (1) Å, and Z = 8. The crystal structure was refined to final residuals of R = 0.0334 and R_w = 0.0450. The pseudotetrahedral molecule has crystallographic C_2 symmetry. It contains two bent, Z-configurated thiazato ligands, the NSO angle being 119.1 (3)°. The NS and SO distances (1.483 (4) and 1.450 (6) Å, respectively) correspond to a cumulated NSO π-system. With the methyl- and pentamethyl-substituted derivatives, the complexes (η^5-C_5H_4Me)$_2$TiCl(NSN-*t*-Bu) (**3**), (η^5-C_5Me_5)$_2$Ti(NSN-*t*-Bu)$_2$ (**4**), and (η^5-C_5H_4Me)$_2$Ti(NSO)$_2$ (**6**) were isolated and characterized.

Introduction

As SO_2 analogues, both the sulfur diimide anion [NSNR]$^-$ and the thiazate anion, [NSO]$^-$, possess a cumulated π-system along a bent three-atom backbone.



In contrast to the rich coordination chemistry of the neutral parent systems RNSNR[2-11] and RNSO,[11-16] only one single example for each NSNR and NSO complexes have been established up to now. The sulfurdiimido complex $(Ph_3P)_2Pt(NSNSiMe_3)_2$ was obtained by reacting $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ with bis(trimethylsilyl)sulfur diimide,[17] and the thiazato compound $(Ph_3P)_2Rh(CO)(NSO)$ was isolated from the reaction of $(Ph_3P)_3Rh(CO)H$ with $CsNSO_2$.[18] We now report a straightforward synthesis of titanium sulfur diimide complexes starting from K[NSN-*t*-Bu] and their hydrolysis on silica to give titanium thiazate complexes.

Experimental Section

All preparations and operations were carried out under purified argon by using conventional Schlenk techniques. Solvents were distilled and saturated with argon. The silica (Merck 60) was deoxygenated under high vacuum and saturated with argon prior to use. The starting materials, (η^5-C_5H_5)$_2$TiCl$_2$,[19] (η^5-C_5H_4Me)$_2$TiCl$_2$,[20] (η^5-C_5Me_5)$_2$TiCl$_2$,[21] and K[NSN-*t*-Bu],[22] were prepared according to published methods.

The infrared spectra were recorded on a Perkin-Elmer 983 G instrument; the ^{1}H and ^{13}C NMR spectra were run on a JEOL FX 90Q spectrometer. The NMR measurements were performed at -20 °C unless stated otherwise.

Synthesis of (η^5-C_5H_5)$_2$TiCl(NSN-*t*-Bu) (1). A solution of (η^5-C_5H_5)$_2$TiCl$_2$ (400 mg, 1.6 mmol) in THF (50 mL) was added to a stirred suspension of K[NSN-*t*-Bu] (250 mg, 1.6 mmol) in THF (50 mL) at -78 °C. After 20 min the reaction mixture was allowed to warm up to 0 °C, and the stirring was continued for 3 h. The solvent was evaporated (at 0 °C) and the residue was extracted with *n*-pentane (100 mL). The *n*-pentane solution was filtered through dehydrated Na_2SO_4 and concentrated until crystallization occurred. When the mixture was cooled to -78 °C, precipitation of **1** was complete. The microcrystalline solid was isolated by decanting the solution, and recrystallization from *n*-pentane gave yellow crystals of **1**: yield 126 mg (24%); mp 113-120 °C dec. IR (KBr): 1183 vs, 1078 m cm^{-1} (ν(NSN)). ^{1}H NMR (CDCl$_3$): δ 6.17 (s, C_5H_5), 1.37 (s, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$): δ 115.3 (C_5H_5), 60.8 (*C*(CH$_3$)$_3$), 30.4 (C(*C*H$_3$)$_3$).

Synthesis of (η^5-C_5H_5)$_2$Ti(NSN-*t*-Bu)$_2$ (2). At -40 °C a solution of 375 mg (1.5 mmol) of (η^5-C_5H_5)$_2$TiCl$_2$ in 60 mL of THF was added dropwise to a stirred suspension of K[NSN-*t*-Bu] (470 mg, 3.0 mmol) in THF (80 mL) over a period of 45 min. Then the mixture was allowed to warm up and stirred for 3 h at room temperature. After evaporation of the solvent, the residue was extracted with *n*-pentane (140 mL), and the extract was filtered through dehydrated Na_2SO_4. The solution was concentrated until it became cloudy; the precipitate was filtered off and discarded. Yellow crystals of **2** were obtained upon cooling the clear solution to -78 °C; they were purified by recrystallization from *n*-pentane: yield 343 mg (70%); mp 100-102 °C dec. IR (KBr): 1241 s, 1163 vs cm^{-1} (ν(NSN)). ^{1}H NMR (CDCl$_3$): δ 6.02 (s, C_5H_5), 1.39 (s, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$, 0 °C): δ 113.3 (C_5H_5), 59.7 (*C*(CH$_3$)$_3$), 31.5 (C(*C*H$_3$)$_3$). Anal. Calcd for $C_{18}H_{28}N_4S_2Ti$: C, 52.42; H, 6.84; N, 13.59; S, 15.55; Ti, 11.61. Found: C, 52.33; H, 6.78; N, 13.0; S, 15.4; Ti, 11.8.

Synthesis of (η^5-C_5H_4Me)$_2$TiCl(NSN-*t*-Bu) (3). The methyl-substituted derivative **3** was prepared in analogy to **1**, starting from 443 mg (1.6 mmol) of (η^5-C_5H_4Me)$_2$TiCl$_2$. Recrystallization from *n*-pentane afforded light orange crystals of **3**: yield 280 mg (49%); mp 94-96 °C dec. IR (KBr): 1185 vs, 1080 m cm^{-1} (ν(NSN)). ^{1}H NMR ($C_6D_5CD_3$): δ 5.66-5.37 (m, $C_5H_4CH_3$), 1.95 (s, $C_5H_4CH_3$), 1.57 (s, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): δ 129.0, 120.2, 116.7, 114.2, 111.8 ($C_5H_4CH_3$), 59.8 (*C*(CH$_3$)$_3$), 30.2 (C(*C*H$_3$)$_3$), 16.1 ($C_5H_4CH_3$). Anal. Calcd for $C_{16}H_{23}ClN_2STi$: C, 53.56; H, 6.46; N, 7.81; S, 8.93; Ti, 13.34. Found: C, 52.95; H, 6.77; N, 7.65; S, 8.78; Ti, 13.5.

Synthesis of (η^5-C_5Me_5)$_2$Ti(NSN-*t*-Bu)$_2$ (4). The preparation of the pentamethyl-substituted derivative **4**, starting from 585 mg (1.5 mmol) of (η^5-C_5Me_5)$_2$TiCl$_2$, followed the procedure described for **2** with slight modifications: The reaction mixture was refluxed for 6 h, and the concentrated, cloudy *n*-pentane extract was cooled to -78 °C in order to precipitate unreacted starting material. After filtration the clear solution was reduced to one-tenth of its volume. Cooling to -78 °C afforded red crystals of **4**, which were recrystallized from *n*-pentane; yield 381 mg (46%). IR (KBr): 1214 vs, 1187 vs, 1163 vs cm^{-1} (ν(NSN)). ^{1}H NMR ($C_6D_5CD_3$, 25 °C): δ 1.85 (s, C_5(CH$_3$)$_5$), 1.36 (s, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR ($C_6D_5CD_3$): δ 121.6 (*C*$_5$(CH$_3$)$_5$), 58.5 (*C*(CH$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$), 12.6 (C_5(*C*H$_3$)$_5$).

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Table I. Crystallographic Data for (η^5-$C_5H_5)_2Ti(NSO)_2$ (**5**)

formula	$C_{10}H_{10}N_2O_2S_2Ti$
fw	302.20
cryst syst	orthorhombic
space group	*Fdd*2
a, Å	29.219 (5)
b, Å	14.153 (3)
c, Å	6.189 (1)
V, Å^3	2559.4
Z	8
μ, cm^{-1}	9.1
D(calcd), g cm^{-3}	1.568
temp	room temp
radiation (λ, Å)	Mo Kα (0.710 69)
θ range, deg	2–25
no. of unique data	620
cryst size, mm	0.10 × 0.13 × 0.13
$R\ (=\sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|)$	0.0334
$R_w\ (=[\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{0.5})$	0.0450
$w\ (=\sigma^2(\|F_o\|) + 0.0022F^2)^{-1}$	
largest shift/esd, final cycle	0.004

Synthesis of (η^5-$C_5H_5)_2Ti(NSO)_2$ (5). A solution of 157 mg (0.36 mmol) of **2** in 45 mL of *n*-pentane was passed through a column containing silica (diameter 2 cm, length 25 cm). After penetration of the solution, the silica was washed subsequently with *n*-pentane (70 mL) and CH_2Cl_2 (70 mL). The product was eluted as a yellow zone by using a mixture of THF/CH_2Cl_2 (1:1). Evaporation the solvent provided **5** as a crystalline yellow solid; yield 74 mg (64%). Single crystals suitable for crystallographic studies were obtained by crystallization from dichloromethane/diethyl ether mixtures. The crystals decompose upon heating over a wide temperature range without melting. IR (KBr): 1232 vs, 1076 m cm^{-1} (ν(NSO)). ^{1}H NMR ($CDCl_3$): δ 6.37 (s, C_5H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 114.4 (C_5H_5). Anal. Calcd for $C_{10}H_{10}N_2O_2S_2Ti$: C, 39.74; H, 3.33; N, 9.27; O, 10.59; S, 21.22. Found: C, 39.79; H, 3.43; N, 9.25; O, 10.8; S, 21.00.

Synthesis of (η^5-$C_5H_4Me)_2Ti(NSO)_2$ (6). Dropwise addition of a solution of (η^5-$C_5H_4Me)_2TiCl_2$ (222 mg, 0.8 mmol) in THF (35 mL) to a stirred suspension of 250 mg (1.6 mmol) of K[NSN-*t*-Bu] in THF (45 mL) at −78 °C was followed by refluxing the mixture for 3 h. Then the solvent was evaporated, and the residue was extracted with *n*-pentane (100 mL). After filtration through dehydrogenated Na_2SO_4, the *n*-pentane solution was concentrated to 50 mL and passed over a column filled with silica (diameter 2 cm, length 25 cm). Workup following the procedure described for **5** afforded yellow needlelike crystals of **6**: yield 31 mg (12%); mp 127–130 °C dec. IR (KBr): 1241 vs, 1069 m cm^{-1} (ν(NSO)). ^{1}H NMR ($CDCl_3$): δ 6.18 (m, $C_5H_4CH_3$), 2.16 (s, $C_5H_4CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 129.9, 117.6, 109.6 ($C_5H_4CH_3$), 15.9 ($C_5H_4CH_3$).

X-ray Crystallographic Analysis of (η^5-$C_5H_5)_2Ti(NSO)_2$ (5). The crystal used in this study was mounted in a Lindemann glass capillary. Diffraction data were collected on a Philips four-circle X-ray diffractometer. The unit cell parameters were obtained from least-squares refinement of the 2θ values for 15 high-angle reflections. The space group, *Fdd*2, was deduced from the systematically absent reflections (*hkl* for $h + k$, $k + l$, $l + h \neq 2n$; $0kl$ for $k + l \neq 4n$; $h0l$ for $h + l \neq 4n$). Crystal data are summarized in Table I, where the conditions for the data collection are also listed. Intensities were measured by using graphite-monochromated Mo Kα radiation and a θ(crystal)–2θ(counter) scan mode. The intensities of the three standard reflections were monitored periodically, and no decrease was observed during the data collection. The data were corrected for Lorentz and polarization effects. An absorption correction was not applied since the crystal fragment used was nearly cube-shaped, and the maximum error resulting from neglect of absorption corrections was estimated to be <2% (transmission factors: max, 0.91; min, 0.89).

The titanium and the sulfur atoms were derived from a Patterson map. The remaining non-hydrogen atoms and, in a later stage, four of the five hydrogen atoms could be seen in difference Fourier maps. The hydrogen atoms were assigned fixed positions (riding on the respective C atoms at a distance of 0.94 Å) and fixed temperature factors (U = 0.10 Å^2). The final refinement, using anisotropic thermal parameters for the non-hydrogen atoms, was based on all 620 reflections. The hydrogen atoms were not refined but were included for the F_c calculations. A final difference Fourier map did not show any chemically significant peaks (density ≤ 0.26 e Å^{-3}). The SHELX program system[23] was used for the calculations. Scattering factors for neutral atoms were taken from ref 24, and values for anomalous dispersion effects for Ti were taken from ref 25. The final atomic parameters are listed in Table II. For the space group *Fdd*2, one has to consider two polarities for the crystal structure, the one just determined and the reversed-polarity structure. However, in view of the limited data set we did not attempt to determine the polarity of the structure.

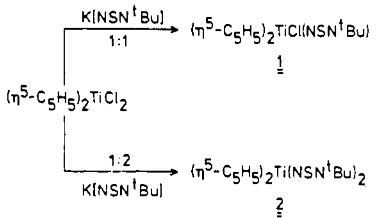
Table II. Positional and Equivalent Isotropic Displacement Parameters (Å^2) for (η^5-$C_5H_5)_2Ti(NSO)_2$[a]

atom	*x*	*y*	*z*	U_{eq}
Ti	0.25	0.25	0.25	0.027 (1)
S	0.1507 (1)	0.2837 (1)	−0.0204 (3)	0.062 (1)
N	0.1996 (1)	0.2681 (3)	0.0328 (7)	0.042 (2)
O	0.1181 (1)	0.2957 (4)	0.1538 (12)	0.110 (4)
C(1)	0.2630 (2)	0.0839 (3)	0.2698 (16)	0.077 (4)
C(2)	0.2179 (2)	0.0963 (4)	0.2344 (14)	0.081 (4)
C(3)	0.2017 (2)	0.1406 (4)	0.4199 (18)	0.103 (5)
C(4)	0.2388 (3)	0.1524 (4)	0.5517 (11)	0.097 (5)
C(5)	0.2759 (2)	0.1206 (4)	0.4498 (13)	0.084 (4)

[a] $U_{eq} = {}^1/_3\sum_{ij}a_1{}^*a_j{}^*a_i{\cdot}a_jU_{ij}$.

Results and Discussion

Reaction of (η^5-$C_5H_5)_2TiCl_2$ with K[NSN-*t*-Bu]. Dicyclopentadienyldichlorotitanium reacts with K[NSN-*t*-Bu] in THF solution under mono- or disubstitution of the chloro ligands. The 1:1 or 1:2 stoichiometry of the reaction can be controlled by using the appropriate molar ratios of the starting compounds. In order to ensure defined conditions, the starting materials were dissolved at −78 °C and then the mixture was warmed up. The synthesis of the bis(sulfur diimido) complex **2** requires higher temperatures than that of the mono(sulfur diimido) compound **1**.



The sulfur diimido complexes **1** and **2** are isolated by crystallization from *n*-pentane. Both compounds are obtained as air-sensitive, microcrystalline solids that dissolve in the usual organic solvents. In the mass spectra, **1** and **2** are characterized by their molecular ions *m/e* 330 and 412, respectively; both signals display the expected isotopic pattern. In the infrared spectra the NSN system in **1** and **2** is recognized by two characteristic bands in the range 1250–1050 cm^{-1}. Both ^{1}H and ^{13}C NMR spectra of **1** exhibit one resonance for the cyclopentadienyl rings and one resonance for the tertiary butyl groups; the signals show no temperature dependence over the range +60 to −80 °C. In principle, four different isomers are possible for **1** according to the *E,E*, *E,Z*, *Z,E*, or *Z,Z* configuration of the cumulated NSN π-system. The simple NMR spectra and the absence of temperature effects suggest that **1** exists only as one isomer, because an isomerization process which is fast with respect to the NMR time scale at −80 °C is unlikely. It is not possible to distinguish between the four different isomers on the basis of the spectroscopic data. However, the majority of sulfur diimides containing alkyl or aryl substituents seem to prefer the *E,Z* configuration in the solid state,[27] as calculated[28] and experimentally established[29] for dimethylsulfur diimide. In solution, a temperature-dependent equilibrium between *E,Z* and *E,E* isomers has been observed in several cases.[27,30] In

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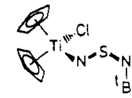
Table III. Bond Distances (Å) and Angles (deg) for $(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$ (**5**)[a]

	Distances		
Ti–N	2.010 (4)	S–N	1.483 (4)
Ti–C(1)	2.381 (7)	S–O	1.450 (6)
Ti–C(2)	2.371 (7)	C(1)–C(2)	1.338 (10)
Ti–C(3)	2.345 (7)	C(2)–C(3)	1.391 (10)
Ti–C(4)	2.346 (7)	C(3)–C(4)	1.367 (10)
Ti–C(5)	2.336 (6)	C(4)–C(5)	1.334 (10)
Ti–Z	2.055	C(5)–C(1)	1.340 (9)
	Angles		
N–Ti–N*	96.0 (2)	C(1)–C(2)–C(3)	107.3 (6)
Z–Ti–Z*	132.7 (3)	C(2)–C(3)–C(4)	106.1 (6)
Ti–N–S	150.8 (3)	C(3)–C(4)–C(5)	108.8 (7)
N–S–O	119.1 (3)	C(4)–C(5)–C(1)	108.4 (6)
C(5)–C(1)–C(2)	109.3 (6)		

[a] Z and Z* are the centroids of the η^5-cyclopentadienyl rings.

view of these findings we assume the *E*,*Z* configuration as the sterically least-hindered geometry of the NSN system in **1**. In contrast to **1**, complex **2** gives rise to NMR spectra that are strongly dependent on temperature and solvent. In $CDCl_3$ solution at −20 °C, the ^1H spectrum shows only two resonances—one for the cyclopentadienyl protons and one for the tertiary butyl protons. In $C_6D_5CD_3$ this simple pattern is observed only above +25 °C; at −60 °C the spectrum exhibits two signals for the C_5H_5 protons and three signals for the $C(CH_3)_3$ protons (Figure 1, see supplementary material). In a similar manner, the expected three ^{13}C signals of **2** (C_5H_5, $\mathit{C}(CH_3)_3$, $C(\mathit{C}H_3)_3$) observed in $C_6D_5CD_3$ at 0 °C are split into eight resonances at −60 °C ($\delta(\mathit{C}_5H_5)$ 113.6, 112.7; $\delta(\mathit{C}(CH_3)_3)$ 60.0, 59.9, 59.1; $\delta(C(\mathit{C}H_3)_3)$ 33.0, 30.0 (broad)). This phenomenon can be explained by the assumption that the solution contains at least two isomers at lower temperatures. With respect to the geometry of the two NSN systems, a total of 10 isomers is possible for **2**.



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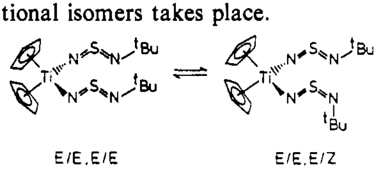
In view of the arguments[27,30] discussed above, we interpret our spectroscopic findings as being consistent with an equilibrium of the *E*,*E*;*E*,*E* and the *E*,*E*;*E*,*Z* isomers of **2** in solution. While at −60 °C both isomers coexist, the simple NMR spectra at room temperature indicate that either the symmetrical *E*,*E*;*E*,*E* configuration is present exclusively or that a rapid interconversion of configurational isomers takes place.



2

Reaction of $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ and $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ with K[NSN-*t*-Bu]. In contrast to $(\eta^5\text{-}C_5H_5)_2TiCl_2$, the ring-substituted methyl and pentamethyl analogues afforded only one product in the reaction with the [NSN-*t*-Bu]$^-$ anion. In the first case only the monosubstitution product $(\eta^5\text{-}C_5H_4Me)_2TiCl(NSN\text{-}t\text{-}Bu)$ (**3**) and in the latter case only the disubstitution product $(\eta^5\text{-}C_5Me_5)_2Ti(NSN\text{-}t\text{-}Bu)_2$ (**4**) could be isolated. While the missing mono(sulfur diimido) complex $(\eta^5\text{-}C_5Me_5)_2TiCl(NSN\text{-}t\text{-}Bu)$ could not be detected by reacting the components in a 1:1 stoichiometry, the bis(sulfur diimido) compound $(\eta^5\text{-}C_5H_4Me)_2Ti(NSN\text{-}t\text{-}Bu)_2$ is supposed to be formed in a refluxing THF solution containing $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ and K[NSN-*t*-Bu] in a molar ratio of 1:2, because this solution can be used to prepare the dithiazato complex **6**. However, the only product isolated by crystallization—irrespective of the stoichiometry—is $(\eta^5\text{-}C_5H_4Me)_2TiCl(NSN\text{-}t\text{-}Bu)$ (**3**).

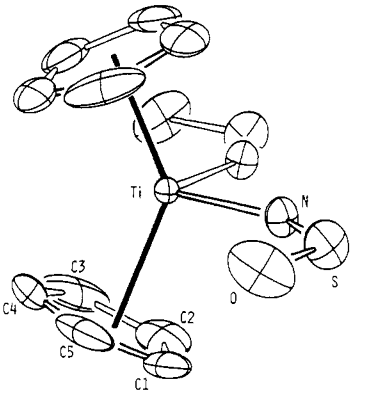


Figure 2. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$ (**5**).

Complexes **3** and **4** crystallize as orange and red solids, respectively, that are sensitive to air. Mass spectra (molecular ions *m*/*e* 358 and 553, respectively) and infrared spectra (two and three ν(NSN) absorptions, respectively), are consistent with their molecular formulas $(\eta^5\text{-}C_5H_4Me)_2TiCl(NSN\text{-}t\text{-}Bu)$ (**3**) and $(\eta^5\text{-}C_5Me_5)_2Ti(NSN\text{-}t\text{-}Bu)_2$ (**4**). In the ^1H NMR spectra **3** gives two singlets for the methyl protons ($C(C\mathit{H}_3)_3$, $C_5H_4C\mathit{H}_3$) and one multiplet for the ring protons ($C_5\mathit{H}_4CH_3$), whereas only two signals ($C_5(C\mathit{H}_3)_5$, $C(C\mathit{H}_3)_3$) are observed for **4**. The ^{13}C NMR spectrum of **3** exhibits five resonances for the ring atoms ($\mathit{C}_5H_4CH_3$), one resonance for the ring-substituted methyl group ($C_5H_4\mathit{C}H_3$), and the expected two signals for the tertiary butyl groups ($\mathit{C}(CH_3)_3$, $C(\mathit{C}H_3)_3$); for **4** four ^{13}C signals ($\mathit{C}_5(CH_3)_5$, $C_5(\mathit{C}H_3)_5$, $\mathit{C}(CH_3)_3$, $C(\mathit{C}H_3)_3$) are observed. Apart from changes in the pattern of the $C_5\mathit{H}_4CH_3$ multiplet in the ^1H NMR spectra of **3**, the NMR signals of **3** and **4** show no dependence on temperature, indicating the absence of isomers. If the arguments discussed for **1** and **2** are applied, the spectroscopic data suggest **3** to exist in the *E*,*E* form and **4** in the *E*,*E*,*E*,*E* configuration.

Hydrolysis of $(\eta^5\text{-}C_5H_5)_2Ti(NSN\text{-}t\text{-}Bu)_2$ (2) on Silica. The bis(sulfur diimido) complex **2** is easily transformed into the bis(thiazato) complex $(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$ (**5**) by hydrolysis on silica. *tert*-Butylamine, presumably produced in this reaction, would be retained on the silica. While the pentamethyl complex **4** is stable toward hydrolysis under these conditions, the methyl-substituted dithiazato derivative $(\eta^5\text{-}C_5H_4Me)_2Ti(NSO)_2$ is accessible by exposing a THF solution containing $(\eta^5\text{-}C_5H_4Me)_2TiCl_2$ and K[NSN-*t*-Bu] (molar ratio 1:2)—that has been refluxed for several hours—to silica.

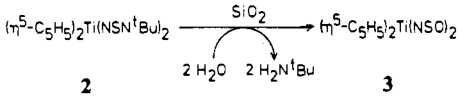
Complex **5**, as well as the methyl analogue **6**, are isolated as air-sensitive, yellow crystals. In the mass spectra, the molecular ions with the expected isotope distribution are observed at *m*/*e* 305 and 330, respectively. The presence of the NSO system in

Table IV. Structural Parameters for $(\eta^5\text{-}C_5H_5)_2TiX_2$ Complexes (X = Ligand Bonded via N)

	dist, Å		angle, deg			
complex	Ti–Z	Ti–N	Z–Ti–Z*	N–Ti–N	at N	ref
$(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$	2.06	2.010 (4)	132.7 (3)	96.0 (2)	151.0 (3)	this work
$(\eta^5\text{-}C_5H_5)_2Ti(NCO)_2$	2.05 2.06	2.007 (3) 2.018 (3)	*b*	94.7 (2)	171.8 (3) 175.7 (3)	33
$(\eta^5\text{-}C_5H_5)_2Ti(NCS)_2$	2.05	2.021 (7)	136.3[c]	93.9 (3)	177.5 (6)	34
$(\eta^5\text{-}C_5H_5)_2Ti(N_3)_2$	2.03 2.06	2.03 (1)	132.2	94.1	137 (1)	35

[a] Z, Z* centroids of C_5 rings. [b] Value not available. [c] Calculated from the atomic coordinates given in ref 34.

5 and **6** is confirmed by comparison of the IR spectra with those of both $(Ph_3P)_2Rh(CO)(NSO)$[18] and of K[NSO].[31]



2 **3**

According to the ^1H and ^{13}C NMR spectra the ring systems in **5** and **6** are equivalent: For **5** only one signal is observed in both the ^1H and ^{13}C NMR spectra. The ^1H NMR spectrum of the methyl-substituted derivative **6** contains a singlet for the methyl protons and a singletlike multiplet for the four remaining ring protons; in the ^{13}C NMR spectrum of **6** a signal for the methyl group and three signals for the different kinds of ring carbon nuclei are observed. The spectra are independent of temperature; therefore, the NMR data suggest either rotation of the two ring systems or the existence of symmetrical rotamers. However, the NMR spectra are not conclusive as to the *E* or *Z* configuration of the NSO moiety, and therefore a X-ray crystallographic structure determination of **5** was carried out. Since no isomerization is observed by NMR spectroscopy, the configuration of **5** and **6** in solution is likely to be the same (*Z*,*Z*) as found for **5** in the solid state.

Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$ (5). Figure 2 shows an ORTEP drawing of a molecule of **5**; bond distances and angles are ~~listed in Table~~ III. They are not corrected for the effects of thermal motion. The scatter in the bond distances for the C_5 ring (1.340 (9)–1.386 (12) Å) reflects its pronounced libration motion. The molecule has crystallographic C_2 symmetry. The atoms of the $Ti(NSO)_2$ moiety are nearly coplanar (deviations (Å) from the N–Ti–N′ plane: S, 0.03; O, 0.02). The centroids of the C_5 rings and the coordinated N atoms define a distorted tetrahedron. The coordination geometry about the titanium atom is very similar to that of many other $(\eta^5\text{-}C_5H_5)_2TiX_2$ complexes. In Table IV $(\eta^5\text{-}C_5H_5)_2Ti(NSO)_2$ (**5**) is compared in particular with other $(\eta^5\text{-}C_5H_5)_2Ti^{IV}$ compounds that contain monodentate ligands bonded via nitrogen atoms. The relatively large Ti–N–S bond angle of 150.8 (3)° in **5** is consistent with the assumption that the Ti–N bond has some double bond character; an extreme formulation for this situation would be Ti=N=S=O.

The view that the titanium atom tends to achieve an effective 18-electron configuration by ligand π-donation has been suggested by Huffman et al. for Ti–Cl and Ti–OR bonds in titanocene derivatives.[32] Judging from the Ti–N bond distances, all complexes listed in Table IV have nearly the same degree of Ti–N π-bonding.

The geometry of the NSO group in **5** agrees within reasonable limits with the geometry of ~~the~~ NSO group in $(Ph_3P)_2Rh(CO)(NSO)$,[18] the values for *d*(N–S), *d*(S–O), and ∠(N–S–O) in the Rh complex being 1.480 (12) Å, 1.509 (10) Å, and 122.5 (5)°. There are no abnormally short intermolecular contacts between individual molecules. Contacts (Å) less than 3.5 Å are as follows: O···S (at $^1/_4 - x$, $^1/_4 + y$, $^1/_4 + z$), 3.44 (1); O···C(2) (at $^1/_4 - x$, $^1/_4 + y$, $^1/_4 + z$), 3.31 (1).

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: ^1H NMR spectra of **2** at –60, –26, and +25 °C (Figure 1) and a complete list of atomic parameters (anisotropic thermal parameters for non-hydrogen atoms and *x*, *y*, *z* values for hydrogen atoms) (2 pages); a table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Complexes of Binucleating Ligands. 20. Complexes of a New, Easily Accessible Binucleating Ligand Containing an Aliphatic Thiolate Bridging Center

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2-(Acetylthio)-*N*,*N*′-bis(pyridin-2-ylmethyl)butanediamide (V) is very simple to synthesize and acts as a convenient precursor to a new type of thiolate-based binucleating ligand, hereafter L^{3-}, represented in the generalized binuclear complex III. Reaction of V with $M(CH_3CO_2)_2$ (M = Pd(II), Ni(II), Cu(II)) leads to rapid metal-promoted S-deprotection and yields $LM_2(\mu\text{-}CH_3CO_2)$ simply and cleanly. $LCu_2(CH_3CO_2)$, a rare example of a dicopper(II) complex with a bridging thiolate center, shows very weak magnetic exchange between the cupric centers. Several diamagnetic Pd^{II}_2 complexes (and some related Ni^{II}_2 complexes) were obtained by substitution of the bridging acetate in the appropriate $LM_2(CH_3CO_2)$ by other carboxylates, pyrazolates, I^-, N_3^-, SCN^-, $RCONH^-$ (the conjugate base of a carboxamide), and $(CH_3)_2NO^-$ (the conjugate base of *N*,*N*-dimethylhydroxylamine) and were studied by ^1H and ^{13}C NMR spectroscopy. Reaction of $LPd_2(CH_3CO_2)$ with NaI gives $(LPd_2I_2)Na$ and with NaN_3 gives $(LPd_2(N_3)_2)Na$, but reaction with NaSCN gives $LPd_2(SCN)$. The relative sluggishness of reaction between $LPd_2(RCO_2)$ and carboxamides, $R'CONH_2$, to give $LPd_2(R'CONH)$ suggests a sterically more congested bridging site in LPd_2^+ than in closely related earlier systems. Because of the asymmetry of L^{3-} geometrical isomeric forms of $LPd_2(R'CONH)$ are possible (VI and VII) and are observed by NMR spectroscopy. Reaction of $LPd_2(CH_3CO_2)$ with *N*,*N*-dimethylhydroxylamine and base gives $LPd_2((CH_3)_2NO)$, which exists in only one of the two possible geometrical isomeric forms and which shows nonequivalent *N*-methyl groups.

Introduction

Complexes of binucleating ligands may provide new sorts of chemistry occurring under the simultaneous influence of two metal centers. Binucleating ligands constructed around a central hinging thiolate center show particular promise in this area for the reasons outlined below. Studies of complexes of the type I[1] and related systems[2] have revealed that the site occupied by Z can accommodate three-atom bridges (e.g. $\mu\text{-}RCO_2^-$), two-atom bridges (e.g.

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