Crystal structure of 1,5-cyclooctadiene-bis[(4-methyl-pyridin-2-yl)-trimethylsilanyl-amido]ruthenium(II), $\text{Ru}(\text{C}_8\text{H}_{12})(\text{C}_9\text{H}_{15}\text{N}_2\text{Si})_2$

S. Deeken, T. Irrgang and R. Kempe*

Universität Bayreuth, Lehrstuhl für Anorganische Chemie II, 95440 Bayreuth, Germany

Received February 8, 2006, accepted and available on-line March 3, 2006; CCDC no. 1267/1733

Abstract

$\text{C}_{26}\text{H}_{42}\text{N}_4\text{RuSi}_2$, monoclinic, $C12/c1$ (no. 15), $a = 16.399(2) \text{ \AA}$, $b = 16.138(2) \text{ \AA}$, $c = 21.349(2) \text{ \AA}$, $\beta = 96.735(7)^\circ$, $V = 5611.0 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.034$, $wR_{\text{ref}}(F^2) = 0.097$, $T = 193 \text{ K}$.

Source of material

To a stirred solution of 0.4 g (2.2 mmol) of lithiated (4-methylpyridin-2-yl)-trimethylsilanyl-amine in 8 mL diethyl ether a suspension of 0.308 g (1.1 mmol) $[(\text{cod})\text{RuCl}_2]$ (cod = 1,5-cyclooctadiene) in 10 mL thf was added at -30°C and the solution was stirred for six hours at this temperature. The reaction mixture was then stored at -25°C over night. The solvent was removed in vacuum and the residue was extracted with hexane and filtered. The yellow-brown filtrate was stored at -25°C to afford yellow crystals suitable for X-ray crystal structure analysis (yield 0.38 g, 61 %).

Discussion

The development of amido metal chemistry of the early transition metals increased dramatically in the last decades. In comparison late transition amido metal chemistry is much less developed [1]. The amido-metal bond in the complexes can be stabilized by additional N-donor functions, for instance by a pyridine moiety [2].

Recently, we have reported examples of amido complexes of late transition metals (nickel and palladium) stabilized by deprotonated 2-aminopyridines [3,4]. The first aminopyridinato complex of ruthenium, a dinuclear complex, was reported by Cotton et al. [5].

The title compound, a mononuclear ruthenium complex, consists of two aminopyridinato ligands and one cod ligand. The bulky trimethylsilyl substituents at the amido N atoms force the aminopyridinato ligands into a *transoid* arrangement. An unusual binding situation is notified by the small chelating angles of 63.00° ($\angle\text{N1-Ru1-N2}$) and of 63.10° ($\angle\text{N3-Ru1-N4}$). Both pyridine rings are in plane with the ruthenium atom and the appropriate amido N atoms. The deviations from the planes are 0.0047 Å and 0.0141 Å. The angle between these planes is 87.3° . For each of the two aminopyridinato ligands, the Ru—N_{pyridine} distance ($d(\text{Ru1-N2}) = 2.071 \text{ \AA}$, $d(\text{Ru1-N4}) = 2.082 \text{ \AA}$) is significantly shorter than the corresponding Ru—N_{amido} distance ($d(\text{Ru1-N1}) = 2.179 \text{ \AA}$, $d(\text{Ru1-N3}) = 2.173 \text{ \AA}$).

Table 1. Data collection and handling.

Crystal:	yellow prism, size $0.05 \times 0.05 \times 0.15 \text{ mm}$
Wavelength:	Mo K_{α} radiation ($0.71069 \text{ \AA}$)
μ :	6.65 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω
$2\theta_{\text{max}}$:	52.44°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	37728, 5568
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4356
$N(\text{param})_{\text{refined}}$:	298
Programs:	SIR97 [6], SHELXL-97 [7]

Table 2. Atomic coordinates and displacement parameters (in $\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	8f	0.7663	0.1751	0.6370	0.043
H(2)	8f	0.8212	0.1423	0.7372	0.044
H(3A)	8f	0.7839	0.0208	0.7870	0.056
H(3B)	8f	0.7135	0.0024	0.7304	0.056
H(4A)	8f	0.6321	0.0345	0.8025	0.054
H(4B)	8f	0.7003	0.0899	0.8424	0.054
H(5)	8f	0.6279	0.2016	0.8017	0.041
H(6)	8f	0.5680	0.2161	0.6995	0.041
H(7A)	8f	0.5383	0.0957	0.6376	0.056
H(7B)	8f	0.5930	0.0408	0.6889	0.056
H(8A)	8f	0.6736	0.0395	0.6121	0.056
H(8B)	8f	0.6443	0.1291	0.5866	0.056
H(10)	8f	0.7566	0.4005	0.5566	0.038
H(12)	8f	0.9700	0.3969	0.6731	0.045
H(13)	8f	0.9090	0.3109	0.7412	0.039
H(14A)	8f	0.9641	0.4760	0.5789	0.072
H(14B)	8f	0.8760	0.5165	0.5582	0.072
H(14C)	8f	0.9051	0.4377	0.5211	0.072

* Correspondence author (e-mail: kempe@uni-bayreuth.de)

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(16)	8f	0.7412	0.3688	0.9137	0.039
H(18)	8f	0.5613	0.4912	0.8042	0.040
H(19)	8f	0.5764	0.3983	0.7230	0.036
H(20A)	8f	0.5991	0.5382	0.9086	0.065
H(20B)	8f	0.6940	0.5254	0.9341	0.065
H(20C)	8f	0.6260	0.4653	0.9575	0.065
H(21A)	8f	0.8913	0.1079	0.8259	0.092
H(21B)	8f	0.9606	0.1405	0.8792	0.092
H(21C)	8f	0.9453	0.1872	0.8128	0.092
H(22A)	8f	0.8612	0.3562	0.9293	0.084
H(22B)	8f	0.9260	0.3471	0.8792	0.084
H(22C)	8f	0.9414	0.3003	0.9456	0.084

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(23A)	8f	0.6763	0.3111	0.4878	0.068
H(23B)	8f	0.5803	0.3061	0.4637	0.068
H(23C)	8f	0.6271	0.2266	0.4950	0.068
H(24A)	8f	0.6347	0.4644	0.5682	0.065
H(24B)	8f	0.5672	0.4541	0.6159	0.065
H(24C)	8f	0.5403	0.4515	0.5415	0.065
H(25A)	8f	0.7592	0.2045	0.9599	0.094
H(25B)	8f	0.8445	0.1563	0.9755	0.094
H(25C)	8f	0.7734	0.1181	0.9261	0.094
H(26A)	8f	0.4852	0.2911	0.6305	0.073
H(26B)	8f	0.5034	0.2140	0.5871	0.073
H(26C)	8f	0.4566	0.2937	0.5562	0.073

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ru(1)	8f	0.70948(2)	0.23202(2)	0.72276(1)	0.0269(1)	0.0252(1)	0.0246(1)	0.0011(1)	0.00509(9)	0.0006(1)
Si(2)	8f	0.59940(6)	0.32128(6)	0.57563(4)	0.0321(5)	0.0371(5)	0.0265(4)	0.0026(4)	0.0016(4)	-0.0002(4)
Si(1)	8f	0.84209(6)	0.22589(7)	0.87669(5)	0.0376(5)	0.0461(6)	0.0330(5)	0.0034(4)	-0.0022(4)	0.0083(4)
N(1)	8f	0.7654(2)	0.2557(2)	0.8188(1)	0.033(1)	0.034(1)	0.026(1)	0.004(1)	0.002(1)	0.001(1)
N(3)	8f	0.6778(2)	0.2950(2)	0.6333(1)	0.031(1)	0.029(1)	0.024(1)	-0.002(1)	0.004(1)	0.001(1)
N(4)	8f	0.8007(2)	0.3039(2)	0.6896(1)	0.030(1)	0.029(1)	0.027(1)	0.001(1)	0.005(1)	-0.001(1)
C(1)	8f	0.7391(2)	0.1342(2)	0.6589(2)	0.049(2)	0.028(2)	0.034(2)	0.006(1)	0.014(2)	-0.007(1)
C(2)	8f	0.7735(2)	0.1133(2)	0.7195(2)	0.045(2)	0.025(2)	0.040(2)	0.009(1)	0.009(2)	0.000(1)
C(3)	8f	0.7385(3)	0.0462(2)	0.7589(2)	0.061(2)	0.027(2)	0.053(2)	0.008(2)	0.011(2)	0.009(2)
C(4)	8f	0.6734(3)	0.0785(2)	0.7993(2)	0.058(2)	0.032(2)	0.045(2)	-0.005(2)	0.011(2)	0.010(2)
N(2)	8f	0.6661(2)	0.3330(2)	0.7687(1)	0.029(1)	0.029(1)	0.024(1)	0.000(1)	0.002(1)	0.000(1)
C(5)	8f	0.6299(2)	0.1559(2)	0.7739(2)	0.037(2)	0.030(2)	0.037(2)	-0.009(1)	0.012(1)	0.004(1)
C(6)	8f	0.5928(2)	0.1647(2)	0.7125(2)	0.032(2)	0.033(2)	0.039(2)	-0.010(1)	0.006(1)	0.001(1)
C(7)	8f	0.5909(3)	0.0939(2)	0.6656(2)	0.055(2)	0.036(2)	0.047(2)	-0.013(2)	-0.001(2)	-0.005(2)
C(8)	8f	0.6616(3)	0.0966(2)	0.6252(2)	0.065(3)	0.032(2)	0.042(2)	-0.001(2)	0.005(2)	-0.011(2)
C(9)	8f	0.7536(2)	0.3289(2)	0.6362(1)	0.030(2)	0.028(2)	0.025(2)	0.002(1)	0.006(1)	-0.003(1)
C(10)	8f	0.7885(2)	0.3822(2)	0.5941(2)	0.038(2)	0.032(2)	0.025(2)	0.000(1)	0.007(1)	-0.001(1)
C(11)	8f	0.8693(2)	0.4076(2)	0.6075(2)	0.039(2)	0.029(2)	0.033(2)	-0.005(1)	0.014(1)	-0.006(1)
C(12)	8f	0.9145(2)	0.3802(2)	0.6630(2)	0.031(2)	0.040(2)	0.042(2)	-0.007(1)	0.008(1)	-0.005(2)
C(13)	8f	0.8782(2)	0.3289(2)	0.7031(2)	0.026(2)	0.037(2)	0.035(2)	0.002(1)	0.004(1)	-0.002(1)
C(14)	8f	0.9069(3)	0.4645(3)	0.5625(2)	0.052(2)	0.049(2)	0.047(2)	-0.014(2)	0.017(2)	0.001(2)
C(15)	8f	0.7160(2)	0.3218(2)	0.8236(2)	0.029(2)	0.033(2)	0.026(2)	-0.001(1)	0.006(1)	0.002(1)
C(16)	8f	0.7078(2)	0.3759(2)	0.8747(2)	0.037(2)	0.037(2)	0.024(2)	-0.006(1)	0.007(1)	-0.002(1)
C(17)	8f	0.6508(2)	0.4391(2)	0.8674(2)	0.037(2)	0.031(2)	0.034(2)	-0.008(1)	0.013(1)	-0.006(1)
C(18)	8f	0.6010(2)	0.4481(2)	0.8100(2)	0.033(2)	0.029(2)	0.038(2)	0.003(1)	0.011(1)	-0.001(1)
C(19)	8f	0.6105(2)	0.3931(2)	0.7620(2)	0.030(2)	0.029(2)	0.031(2)	0.001(1)	0.007(1)	0.000(1)
C(20)	8f	0.6417(2)	0.4971(2)	0.9216(2)	0.051(2)	0.040(2)	0.041(2)	-0.007(2)	0.017(2)	-0.011(2)
C(21)	8f	0.9189(3)	0.1572(3)	0.8449(2)	0.049(2)	0.069(3)	0.062(3)	0.020(2)	-0.008(2)	0.005(2)
C(22)	8f	0.8995(3)	0.3184(3)	0.9119(2)	0.042(2)	0.070(3)	0.053(3)	-0.003(2)	-0.009(2)	0.004(2)
C(23)	8f	0.6237(3)	0.2872(3)	0.4961(2)	0.054(2)	0.051(2)	0.030(2)	-0.001(2)	0.001(2)	-0.005(2)
C(24)	8f	0.5835(2)	0.4366(2)	0.5753(2)	0.047(2)	0.044(2)	0.041(2)	0.011(2)	0.010(2)	0.007(2)
C(25)	8f	0.7997(3)	0.1695(3)	0.9424(2)	0.076(3)	0.072(3)	0.037(2)	-0.010(2)	-0.006(2)	0.019(2)
C(26)	8f	0.4993(2)	0.2745(3)	0.5889(2)	0.039(2)	0.059(3)	0.046(2)	-0.002(2)	-0.001(2)	0.006(2)

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support.

References

- Kempe, R.: Highlights in the Renaissance of Amidometal Chemistry. *Angew. Chem., Int. Ed.* **39** (2000) 468-493.
- Kempe, R.: The Strained μ_2 -N-Amido-N-Pyridine Coordination of Aminopyridinato Ligands. *Eur. J. Inorg. Chem.* (2003) 791-803.
- Spannenberg, A.; Arndt, P.; Kempe, R.: Yttrate-Mediated Ligand Transfer and Direct Synthesis as a Route to Amidopalladium Complexes. *Angew. Chem., Int. Ed.* **37** (1998) 832-835.
- Deeken, S.; Proch, S.; Casini, E.; Braun, H. F.; Mechtler, C.; Marschner, C.; Motz, G.; Kempe, R.: Group 10 Metal Aminopyridinato Complexes: Synthesis, Structure, and Application as Aryl-Cl Activation and Hydro-silane Polymerization Catalysts. *Inorg. Chem.* **45** (2006) 1871-1879.
- Chakravarty, A. R.; Cotton, F. A.; Tocher, D. A.: Synthesis and molecular structure of Ru₂(C₅NH₄NH)₆(PMe₂Ph)₂, a ruthenium-ruthenium-bonded molecule with 2-pyridinylamide ligands in three coordination modes and other novel features. *Inorg. Chem.* **23** (1984) 4030-4033.
- Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R.: SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **32** (1999) 115-119.
- Sheldrick, G. M.: SHELXL-97, Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.