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Experimental and Theoretical Investigations on the Catalytic Hydrosilylation of Carbon Dioxide with Ruthenium Nitrile Complexes

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The molecular structures of *cis*-RuCl₂(MeCN)₄, **7**, and *trans*-RuBr₂(MeCN)₄, **10**, were determined by X-ray crystallography.

All diffraction data were collected on a Siemens SMART 1000 CCD diffractometer (Table 1). A full sphere of data was collected with an irradiation time of 10 s to 20 s per frame using an ω -scan technique.

Table 1. Crystallographic data of complexes **7**·(MeCN)₂ and **10** (standard deviations in parentheses).

Complex	7	10
Empirical formula	C ₈ H ₁₂ Cl ₂ N ₄ Ru·* 2 C ₂ H ₃ N	C ₈ H ₁₂ Br ₂ N ₄ Ru
Formula weight	336.36	425.10
Crystal size (mm ³)	0.3 x 0.3 x 0.04	0.1 x 0.05 x 0.05
Crystal system	orthorhombic	orthorhombic
Space group	Cmc2(1) (No. 36)	Pbca (No. 61)
Unit cell dimensions	a = 17.3370(15) b = 7.7022(6) c = 13.9083(10)	a = 12.2222(10) b = 8.6866(7) c = 12.9999(11)
Volume (Å ³)	1857.2(3)	1380.2(2)
Z	Z = 4	Z = 4
Density (calculated) (Mg/m ³)	1.496	2.046
Diffractometer	Siemens SMART 1000 CCD diffractometer	
Wavelength	MoK α , graphite monochromator	
Temperature (K)	200(2)	200(2)
θ range	2.35 $\leq \theta \leq$ 28.33°	3.13 $\leq \theta \leq$ 28.29°
Scan	ω scan, $\Delta \omega=0.4^\circ$	ω scan, $\Delta \omega=0.4^\circ$
Index ranges	-22 $\leq h \leq$ 22, -10 $\leq k \leq$ 10, -18 $\leq l \leq$ 18	-16 $\leq h \leq$ 16, -11 $\leq k \leq$ 11, -17 $\leq l \leq$ 17
Number of reflections measured	10971 (C-cell)	15386
Independent reflections	2349	1712
Reflections observed	1870 (I > 2 σ)	1057 (I > 2 σ)
Number of parameters refined	110	73
Residual electron density (e pm ⁻³)	0.63 10 ⁻⁶	1.37 10 ⁻⁶
Corrections	Lorentz and polarization, exp. absorption correction	
Structure solution	Direct methods	
Structure refinement	Full-matrix least-squares on F ²	
Programs and weightings used	SHELX-97, ^[1] XPMA and WINRAY, ^[2]	
R indices	R ₁ = 0.0359 (I > 2 σ) R _w = 0.0806 (all data against F ²)	R ₁ = 0.0418 (I > 2 σ) R _w = 0.1156 (all data against F ²)

CCDC 292278 (**7**) and CCDC 292277 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The yellow-orange complex **7** (Figure 1) crystallizes out of the reaction solution, the purple complex **10** (Figure 2) out of MeCN. In both complexes, all MeCN ligands are coordinated end-on to the ruthenium centers, with Ru-N bond distances not far from the sum of estimated single covalent radii (~ 2.00 Å),^[3] indicating little $d\pi$ - $p\pi$ backbonding. Also in both structures, half of the molecule is in the independent unit of the elementary cell, the other half generated by a crystallographic mirror plane (**7**) and inversion center (**10**), respectively.

Figure 1. Molecular structure of complex **7**; Bond lengths [Å] and angles [°]: Ru(1)-N(2) 1.970(2), Ru(1)-N(3) 2.011(3), Ru(1)-N(3a) 2.011(3), Ru(1)-N(1) 2.090(2), Ru(1)-Cl(1a) 2.4052(9), Ru(1)-Cl(1) 2.4052(9), N(1)-C(1) 0.99(4), N(2)-C(3) 1.26(3), N(3)-C(5) 1.135(5), N(4)-C(7) 1.135(9), C(1)-C(2) 1.46(3), C(3)-C(4) 1.44(3), C(5)-C(6) 1.471(5), C(7)-C(8) 1.460(9), N(2)-Ru(1)-N(3) 89.5(6), N(3)-Ru(1)-N(3a) 93.24(16), N(2)-Ru(1)-N(1) 177.4(2), N(3)-Ru(1)-N(1) 88.7(6), N(3a)-Ru(1)-N(1) 88.7(6), N(2)-Ru(1)-Cl(1a) 89.9(4), N(3)-Ru(1)-Cl(1a) 178.8(3), N(3a)-Ru(1)-Cl(1a) 87.84(8), N(1)-Ru(1)-Cl(1a) 92.0(4), N(2)-Ru(1)-Cl(1) 89.9(4), N(3)-Ru(1)-Cl(1) 87.84(8), N(3a)-Ru(1)-Cl(1) 178.8(3), N(1)-Ru(1)-Cl(1) 92.0(4), Cl(1a)-Ru(1)-Cl(1) 91.06(5), C(1)-N(1)-Ru(1) 173.0(19), C(3)-N(2)-Ru(1) 173.2(15), C(5)-N(3)-Ru(1) 175.8(7), N(1)-C(1)-C(2) 178(2), N(2)-C(3)-C(4) 179.5(18), N(3)-C(5)-C(6) 178.7(15), N(4)-C(7)-C(8) 161(2).

The six-coordinated ruthenium atom in complex **7** (Figure 1) has a distorted octahedral geometry and is one of the rare examples of complexes of the cis - $L_2Ru^{II}(RCN)_4$ type^[3, 4] and the first complex structurally reported of the cis - $Ru^{II}X_2(RCN)_4$ (X =halide) type. Probably due to packing forces, the two MeCN ligands in **7** *trans* to each other, are bent away from the $RuCl_2$ fragment: The N1–Ru–N2 bond angle is $177.4(2)^\circ$, and the Ru-N1-C1 and Ru-N2-C3 angles are $173.0(19)^\circ$ and $173.2(15)^\circ$, respectively. A similar bent structure was reported for $Ru^{II}(cod)(RCN)_4^{2+}$.^[4] The astonishingly big difference of the distances (Ru-N2: 1.970(2) Å;

Ru-N1 2.090(2) Å) in **7** is probably due to errors in the localization of atoms N1 and N2 and therefore not significant, as well as the corresponding N-C distances (N1-C1: 0.990(40) Å; N2-C3: 1.260(30) Å).

Figure 2. Molecular structure of complex **10**; Bond lengths [Å] and angles [°]: Ru(1)-N(1) 2.029(4), Ru(1)-N(1a) 2.029(4), Ru(1)-N(2a) 2.030(5), Ru(1)-N(2) 2.030(5), Ru(1)-Br(1) 2.5438(6), Ru(1)-Br(1a) 2.5438(6), N(1)-C(1) 1.122(7), N(2)-C(3) 1.109(6), C(1)-C(2) 1.475(8), C(3)-C(4) 1.474(7), N(1)-Ru(1)-N(1a) 180, N(1)-Ru(1)-N(2a) 93.55(17), N(1a)-Ru(1)-N(2a) 86.45(17), N(1)-Ru(1)-N(2) 86.45(17), N(1a)-Ru(1)-N(2) 93.55(17), N(2a)-Ru(1)-N(2) 180, N(1)-Ru(1)-Br(1) 89.67(13), N(1a)-Ru(1)-Br(1) 90.33(13), N(2a)-Ru(1)-Br(1) 89.39(13), N(2)-Ru(1)-Br(1) 90.61(13).

Complex **10** (Figure 2) has a *trans*-octahedral coordination geometry with four MeCN ligands in the equatorial positions and two Br ligands in the axial positions. The molecule is isostructural to *trans*-Ru^{II}Cl₂(MeCN)₄ **9**.^[5] Bond angles and bond distances for Ru-N, N-C and C-C are comparable. The Ru-Br distance of complex **10** (2.544 Å) is in the range typical of L_nRu^{II}-Br complexes,^[6] whereas the average Ru-N distance in complex **10** (2.029 Å) is comparable to that in **9** (2.025 Å).^[5] As is reported for several other complexes with end-on coordinating MeCN ligands,^[7] the average C-N distance in the coordinated MeCN molecules (1.115 Å) is formally shorter than the C-N distance in non coordinated MeCN (1.157 Å),^[8] as is commonly observed in transition metal complexes.^[9] The coordinated MeCN in complex **10** is slightly bent (178.6°).

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