idazole or imidazolato group from a cysteine and histidine residue, respectively, of the protein are the most favorable candidates for the axial ligands in the active site of native nitrile hydratase in the ferric low-spin state.

Further characterization of the present model complexes is under way by Mössbauer, EXAFS, and X-ray structure analysis methods.

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# Siloxyl-Bridged Diruthenium(II) Complexes: Structural Models for Cluster-Derived, Silica-Supported Ruthenium Catalysts

*Sir:*

Transition-metal catalysts dispersed on high-surface-area oxides are essential to the operation of many industrial processes, and accordingly the structure and performance of such materials is an area of continuing speculation and study. Understanding surface geometry, in particular the way in which reactive metal centers are bound to a support, is regarded as a primary objective;[1] however, owing to the rarity of suitable molecular models, the current state of knowledge concerning metal–support interactions rests almost entirely on indirect characterization using various spectroscopic techniques.[2] Recently the X-ray crystal structure of the *triangulo*-triosmium derivative $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OSiEt_3)]$ (**1**) was projected as "the first molecular analogue of the silica surface cluster"[3] and has since been related specifically to EXAFS analysis of alumina-supported osmium clusters.[4] We have used X-ray diffraction to determine the structures for two new siloxyl-bridged diruthenium complexes, providing reference parameters for oxide-supported ruthenium catalysts, which are numerous[5] but for which no suitable molecular models have previously been described. In either compound two low-valent Ru atoms are held adjacent but are not bonded to each other (as are the Os centers[3] in **1**): such a configuration is likely to parallel the result of cluster fragmentation[4] that accompanies catalyst activation.

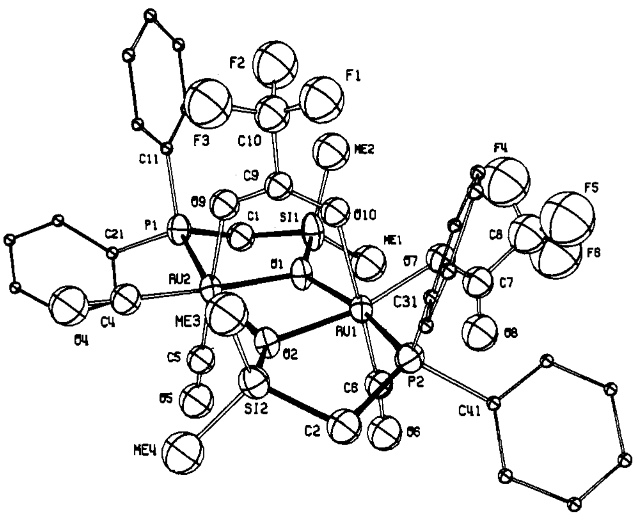


**Figure 1.** ORTEP drawing of compound **4**. Selected bond distances (Å) and angles (deg): Ru(1)–O(1), 2.135 (7); Ru(1)–O(2), 2.091 (6); Ru(2)–O(1), 2.087 (6); Ru(2)–O(2), 2.111 (7); Ru(1)–O(7), 2.085 (7); Ru(1)–O(10), 2.183 (7); Ru(2)–O(9), 2.118 (7); Ru(1)–P(2), 2.262 (3); Ru(2)–P(1), 2.321 (3); Ru(1)–O(1)–Ru(2), 100.5 (3); Ru(1)–O(2)–Ru(2), 101.2 (3); O(1)–Ru(1)–O(2), 77.8 (2); O(1)–Ru(2)–O(2), 78.4 (3); P(2)–Ru(1)–O(2), 89.3 (2); P(1)–Ru(2)–O(1), 87.3 (2). The two Ru centers lie 3.247 (1) Å apart.

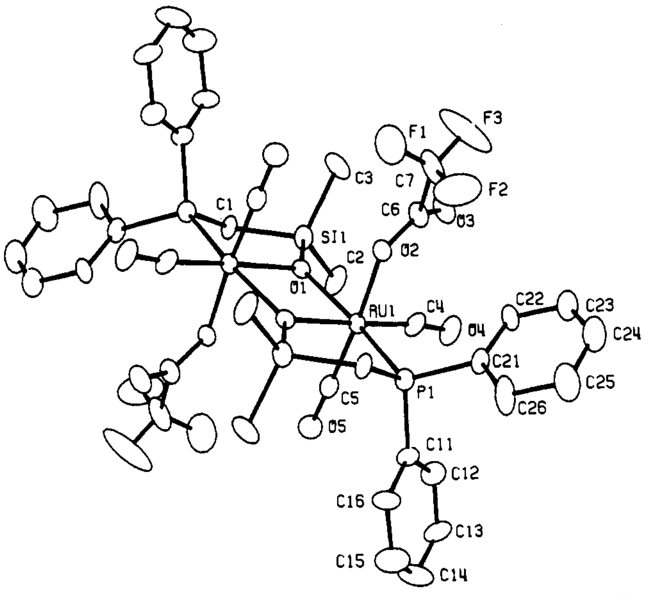
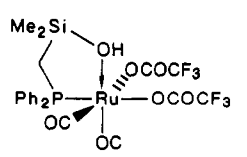


**Figure 2.** ORTEP drawing of compound **6**. Selected bond distances (Å) and angles (deg): Ru(1)–O(1), 2.135 (10); Ru(1)–O(2), 2.086 (12); Ru(1)–P(1), 2.325 (5); Ru(1)–O(1)–Si(1), 135.4 (6); O(1)–Ru(1)–P(1), 165.1 (3); P(1)–Ru(1)–C(4), 94.4 (5); Ru(1)–O(1)–R u(1)′ = 103.0 (4). The two Ru centers lie 3.313 (1) Å apart.

NMR evidence for enhanced acidity of the silanol hydrogen in the unusual complex[6] **2** vs that in $Ru(\eta\text{-}cym)Cl_2(PPh_2CH_2SiMe_2OH)$ (**3**; cym = *p*-cymene; the silanol O is not attached to Ru[7]) suggested that treatment of **2** with $H^-$ might generate a reactive, coordinatively unsaturated siloxy–Ru species via hydrogen loss and ejection of $CF_3CO_2^-$. During an appropriate experiment gas evolution was indeed observed (KH, 1 mol equiv;



**2**

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THF solution) and was followed after addition of hexane (equal volume) by slow (12 h) deposition of bright yellow crystals. This product was shown by using X-ray diffractometry[8] to be the binuclear complex $Ru_2(CO)_3(OCOCF_3)(\mu\text{-}OSiMe_2CH_2PPh_2)_2(\mu\text{-}OCOCF_3)$ (**4**): the molecular structure is illustrated in Figure 1. Simultaneously it was discovered that synthesis[6] of complex **2** by action of $CF_3CO_2H$ on $[Ru(CO)_3(\mu\text{-}SiMe_2CH_2PPh_2)]_2$ (**5**) is accompanied by formation of a minor constituent (<10%), which was obtained as colorless crystals: this was identified as $[Ru(CO)_2(OCOCF_3)(\mu\text{-}OSiMe_2CH_2PPh_2)]_2$ (**6**) (also by X-ray structure determination;[9] see Figure 2), a potential precursor to **4**. Accordingly UV irradiation of **6** (THF solution) rapidly (5 min) affords **4**, although no **6** was observed after exposure of **4** to CO (18 h, ca. 800 psig).

The asymmetric structure of compound **4**, which is evident from the NMR data[8] (diastereotopic methyl groups and methylene hydrogens), is derived from that of **6** by entry of a terminal ester group to displace CO at the second Ru center, forming an unsymmetrical bridge to the latter (Ru–O = 2.12, 2.18 Å; cf. 2.09 Å to the residual terminal ester). Smaller differences in Ru–O distances to the bridging siloxyl fragments compensate one another (2.09, 2.14 vs 2.11, 2.09 Å), and the overall geometry is consistent with formal Ru(II) character for both metal atoms, a conclusion that is self-evident in the structure of **6** under the constraints of crystallographic symmetry. The $Ru_2$ distances of 3.247 (**4**) and 3.313 Å (**6**) both lie outside bonding range; i.e. the molecules model "broken-up" Ru clusters on a silica surface.[4] Most significantly, the Ru–O distances (2.14 Å, **6**; mean 2.11 Å, **4**) confirm that the estimate[10] of 2.17 Å from EXAFS data for a decomposed ruthenium cluster on alumina is essentially correct, reinforce the assertion[4] that "EXAFS results are in agreement with those obtained from X-ray diffraction", and imply directly that in catalytically active surface entities formed by attachment of Ru(0) at an oxide support "the oxidation state of the ruthenium atoms...is different from zero".[4] Further investigation of relationships between complexes **2**–**6** is in progress (in particular formation of **4** from **2**, which appears to involve dimerization of a reactive mononuclear species as projected above and parallels the role of surface Si–OH in formation of oxidized metal centers[11]); it is anticipated that attachment of alkyl or alkenyl ligands at Ru in these new systems will provide information on how the chemistry of hydrocarbon assembly[12] is influenced by electronic characteristics of the oxide surface.

**Acknowledgment.** We thank the NSERC for financial support, including an infrastructure grant for X-ray crystallography, and K. A. Beveridge, R. D. Brost, and Dr. G. W. Bushnell for assisting with the structure determinations.

**Supplementary Material Available:** For compounds **4** and **6**, tables of crystallographic parameters, fractional atomic coordinates, temperature parameters, and bond distances and angles (9 pages); tables of structure factors (21 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for compound **4**: $C_{37}H_{36}F_6O_9P_2Ru_2Si_2$; $M_r$ = 1058.9; triclinic; space group $P1$; $a$ = 9.166 (2) Å, $b$ = 13.718 (2) Å, $c$ = 18.096 (3) Å; $\alpha$ = 110.73 (3)°, $\beta$ = 90.50 (2)°, $\gamma$ = 94.73 (2)°; $V$ = 2119 Å$^3$; $Z$ = 2; $D_{calcd}$ = 1.67 g cm$^{-3}$; Nonius CAD4 diffractometer; Mo K$\alpha$ ($\lambda$ = 0.71069 Å) radiation, $\mu$ = 8.19 cm$^{-1}$; 4818 unique reflections refined to a conventional $R$ = 0.070 ($R_w$ = 0.073). Selected spectroscopic data are as follows. IR (cm$^{-1}$): 2065, 2000, 1952 ($\nu_{CO}$); 1690, 1650 ($\nu_{C=O(ester)}$). $^1$H NMR ($CDCl_3$ solution, $\delta$ vs TMS): −0.03 (s, 3 H), 0.03 (s, 3 H), 0.17 (s, 3 H), 0.36 (s, 3 H), 1.50 (t, 1 H), 1.63 (t, 1 H), 1.73 (t, 1 H), 1.87 (t, 1 H), 7.3–7.8 (m, 20 H). $^{31}$P NMR ($CDCl_3$ solution, $\delta$ vs TMP): −77.7 (s), −93.5 (s).

(9) Crystal data for compound **6**: $C_{38}H_{36}F_6O_{10}P_2Ru_2Si_2$; $M_r$ = 1086.9; monoclinic; space group $P2_1/n$; $a$ = 12.696 (6) Å, $b$ = 15.320 (5) Å, $c$ = 11.343 (5) Å; $\beta$ = 92.31 (3)°; $V$ = 2205 Å$^3$; $Z$ = 2; $D_{calcd}$ = 1.64 g cm$^{-3}$; Nonius CAD4 diffractometer; Mo K$\alpha$ ($\lambda$ = 0.71069 Å) radiation, $\mu$ = 8.47 cm$^{-1}$; 1262 unique reflections refined to a conventional $R$ = 0.060 ($R_w$ = 0.057). Selected spectroscopic data are as follows. IR (cm$^{-1}$): 2065, 2001 ($\nu_{CO}$); 1687 ($\nu_{C=O(ester)}$). $^1$H NMR ($CDCl_3$ solution, $\delta$ vs. TMS): 0.26 (s, 3 H), 0.52 (s, 3 H), 1.65 (t, 1 H), 2.02 (t, 1 H), 7.3–7.8 (m, 10 H). $^{31}$P NMR ($CDCl_3$ solution, $\delta$ vs TMP): −87.9.

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# Articles

Contribution from the Department of Chemistry and Biochemistry,
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## (Polypyridine)ruthenium(II) Complexes Containing Sulfite, Bisulfite, and Sulfur Dioxide

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Complexes of the type $Ru(bpy)_2(HSO_3)L$, where L is bisulfite, water, and pyridine, have been prepared and the acid–base equilibria of coordinated bisulfite examined. For L = pyridine or water a single equilibrium is observed (p$K$ = 3.7 in both cases), which corresponds to the bisulfite/sulfite equilibrium. Evidence for the presence of the sulfur dioxide complex is observed only in 6 M $H_2SO_4$. These data indicate that sulfur dioxide coordinated to the $Ru(bpy)_2$ moiety is significantly more electrophilic than in the polyammine complexes of ruthenium(II). The complex in which L is bisulfite crystallizes in the monoclinic $P2_1/n$ space group with $a$ = 9.008 (1) Å, $b$ = 21.380 (4) Å, $c$ = 11.151 (1) Å, $\alpha$ = 96.02 (1)°, and $Z$ = 4. When L is pyridine, the crystals are triclinic, $P\bar{1}$, with $a$ = 9.767 (2) Å, $b$ = 10.785 (1) Å, $c$ = 17.626 (5) Å, $\alpha$ = 69.29 (2)°, $\beta$ = 71.41 (2)°, $\gamma$ = 65.64°, and $Z$ = 2. The respective numbers of observed reflections were 1512 and 3737, $R$'s were 0.050 and 0.058, and $R_w$'s were 0.053 and 0.071.

### Introduction

The similarities in the ligating properties of nitric oxide and sulfur dioxide have been well documented in the last two decades.[1] Both of these ligands exhibit at least two different geometries when coordinated, and the preferred geometry appears to depend on the number of d electrons in a similar manner. The tetra- and pentaammine complexes of ruthenium[2] have been particularly

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