Organometallics **2004,** *23,* 4531−4533

Ru(xantsil)(CO)(PCy$_3$): Facile Generation of a Coordinatively Unsaturated Ruthenium(II) Complex Bearing 14 Valence Electrons [xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)]

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Received August 11, 2004

*Summary: Treatment of Ru(xantsil)(CO)(η^6-toluene) (**1**) [xantsil = (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl)] with PCy$_3$ led to the formation of Ru(xantsil)(CO)(PCy$_3$) (**3**), in which the xantsil ligand is bound to the ruthenium center in κ^3(Si,Si,O) fashion. The highly coordinatively unsaturated nature of **3** is indicated by the reaction with CO to give Ru(xantsil)(CO)$_3$(PCy$_3$) (**5**).*

Coordinatively unsaturated organotransition metal complexes are known to be key intermediates in metal complex-mediated homogeneous catalytic reactions. The preparation and isolation of these species as a stable form requires the use of ligands with steric and/or electronic properties capable of stabilizing the complexes.[1] It was shown by Heyn et al. that strongly σ-donating groups such as silyl and hydrido ligands can be effective in stabilizing coordinatively unsaturated complexes.[2] Recently, our group has developed a new type of bis(silyl) chelating ligand, (9,9-dimethylxanthene-4,5-diyl)bis(dimethylsilyl), or "xantsil", which can be coordinated to transition metals in κ^2(Si,Si) or κ^3(Si,Si,O) fashion.[3] The complexation of two electron-releasing silyl groups and an ether oxygen atom in the xanthene core is expected to stabilize the coordinatively unsaturated species generated in the catalytic cycle. This communication reports on the reactions of Ru(xantsil)(CO)(η^6-toluene) (**1**) with tertiary phosphines PR$_3$ to give Ru(xantsil)(CO)(PR$_3$)$_n$ [R = Me (n = 3), Cy (n = 1)]. The highly coordinatively unsaturated nature of the latter is indicated by the reaction of Ru(xantsil)(CO)(PR$_3$) with 2 equiv of CO to give Ru(xantsil)(CO)$_3$(PR$_3$), the structure of which was determined by X-ray diffraction study.

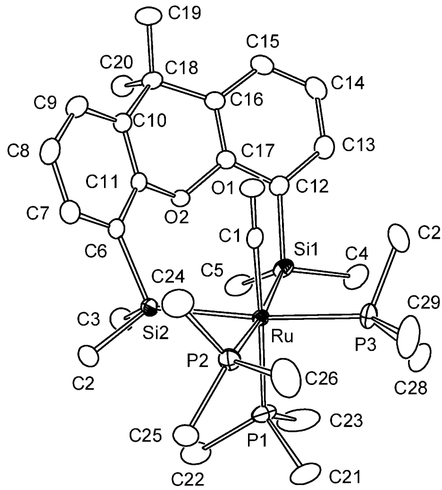

Figure 1. Molecular structure of **2** with thermal ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Ru−C1 1.865(3), Ru−P1 2.4006(9), Ru−P2 2.4004(8), Ru−P3 2.3930(8), Ru−Si1 2.5235(8), Ru−Si2 2.5277(8), C2···C25 3.250(5), C4···C28 3.298(5), Si1−Ru−Si2 91.02(3), C1−Ru−P1 174.89(9), P2−Ru−Si1 173.54(3), P3−Ru−Si2 173.75(3).

The η^6-toluene ligand in **1** was easily substituted by three PMe$_3$ molecules in dichloromethane at room temperature to give Ru(xantsil)(CO)(PMe$_3$)$_3$ (**2**) in 84% yield (eq 1). The molecular structure of **2** was determined by X-ray diffraction study (Figure 1). Complex **2** takes a slightly distorted octahedral geometry in which three incoming PMe$_3$ ligands occupy the *fac*-position. The xanthene core is bent and the dihedral angle between the least-squares planes of two aromatic rings becomes 38.47(13)°. The ruthenium−silicon bonds Ru−Si1 (2.5235(8) Å) and Ru−Si2 (2.5277(8) Å) are unusually long, a structural feature that was also observed in Ru(xantsil)(CO)$_4$ (av 2.565 Å)[3a] and which can be explained similarly by the steric requirement of the xantsil ligand. That is, the rigid xanthene core forces two methyl groups (C3 and C5) to be within an extremely short interatomic distance (3.224(6) Å) compared to the sum of the van der Waals radii of the two methyl groups (4.0 Å). The steric repulsion causes the other methyl groups (C2 and C4) on the silicon atoms to move closer to the methyl groups on the P2 and P3

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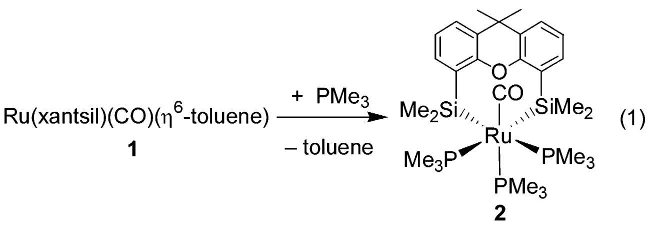
(1) Coordinatively unsaturated complexes: (a) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1988**, 278. (b) Ogasawara, M.; Macgregor, S. A.; Streib, W. E.; Folting, K.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 10189. (c) Gemel, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 5601. (d) Tenorio, M. J.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2000**, *122*, 11230. (e) Yamaguchi, Y.; Nagashima, H. *Organometallics* **2000**, *19*, 725.

(2) Heyn, R. H.; Macgregor, S. A.; Nadasdi, T. T.; Ogasawara, M.; Eisenstein, O.; Caulton, K. G. *Inorg. Chim. Acta* **1997**, *259*, 5.

(3) (a) Tobita, H.; Hasegawa, K.; Minglana, J. J. G.; Luh, L.-S.; Okazaki, M.; Ogino, H. *Organometallics* **1999**, *18*, 2058. (b) Minglana, J. J. G.; Okazaki, M.; Tobita, H.; Ogino, H. *Chem. Lett.* **2002**, 406. (c) Okazaki, M.; Minglana, J. J. G.; Yamahira, N.; Tobita, H.; Ogino, H. *Can. J. Chem.* **2003**, *81*, 1350.

10.1021/om049379e CCC: $27.50
Publication on Web 09/02/2004

phosphines (C2···C25 3.250(5) Å, C4···C28 3.298(5) Å), leading to considerable stretching of the ruthenium−silicon bonds.



(1)

The steric repulsion between the xantsil and PMe$_3$ ligands is reflected in the high lability of the PMe$_3$ ligands. In CD$_2$Cl$_2$, an equilibrium is achieved between **2**, the dissociated PMe$_3$, and **2′** formed through the dissociation of PMe$_3$ (eq 2). This is supported by the observation that when colorless **2** was dissolved in CD$_2$Cl$_2$, the solution turned yellow and the ^{1}H nuclear magnetic resonance (NMR) spectrum exhibited several signals assignable to resonances of **2′** and a broad signal due to free PMe$_3$ in addition to the peaks due to **2**. In the ^{31}P NMR spectrum, three new broad signals were observed at δ −59.4, −6.5, and 27.4. The first peak was assigned to dissociated PMe$_3$, while the last two were assigned to **2′**. The addition of excess PMe$_3$ to the yellow solution shifted the equilibrium in eq 2 to the left to form **2** predominantly, causing the yellow color to disappear. These results are consistent with the formation of Ru(xantsil)(CO)(PMe$_3$)$_2$, although the geometry remains unclear.

$$\underset{\mathbf{2}}{\mathrm{Ru(xantsil)(CO)(PMe_3)_3}} \underset{+\,\mathrm{PMe_3}}{\overset{-\,\mathrm{PMe_3}}{\rightleftharpoons}} \underset{\mathbf{2'}}{\mathrm{Ru(xantsil)(CO)(PMe_3)_2}} \quad (2)$$

Treatment of complex **1** with PCy$_3$ gave Ru(xantsil)(CO)(PCy$_3$) (**3**) in 76% yield. In contrast to **2**, elemental analysis clearly showed that the ruthenium center binds only one PCy$_3$ molecule. All spectroscopic data in CD$_2$Cl$_2$ are also in good agreement with the formation of **3**: The ^{29}Si NMR spectrum exhibits a doublet signal at δ 48.6 coupled with the ^{31}P nuclei ($J_{\mathrm{SiP}} = 39.0$ Hz), whereas the ^{31}P NMR spectrum displays a singlet signal at δ 25.0. In the ^{1}H NMR spectrum, four signals due to methyl groups appear at δ 0.20 (6H, SiMe), 0.51 (6H, SiMe), 1.51 (3H, 9-Me), and 1.80 (3H, 9-Me). No signals were observed in the high-field region typical of the metal-hydrido fragment. The infrared (IR) spectrum includes a strong band at 1876 cm^{-1} assigned to CO stretching vibration. The structure of the model complex, Ru(xantsil)(CO)(P^{i}Pr$_3$), was optimized by density functional theory (DFT) calculations. Complexes **3a** and **3b** were identified as stationary points in the potential energy surface (PES) (Figure 2). The interatomic distances of Ru−O (xanthene) in **3a** and **3b** are 3.264 and 2.284 Å, respectively, indicating the existence of the Ru−O bond in the latter. Accordingly, the former takes a distorted tetrahedral geometry, while the latter takes a distorted square pyramidal geometry with a silyl ligand (Si2) in the apical position. Complex **3b** is lower in energy ($\Delta E = -14.5$ kcal mol^{-1}) than **3a**. Coordination of the ether oxygen atom would compensate for the highly coordinative unsaturation (14 valence electrons for **3a**). Single crystals of **3** suitable for X-ray diffraction study could not be obtained.

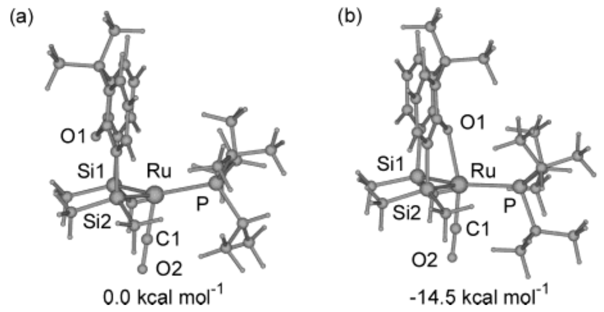
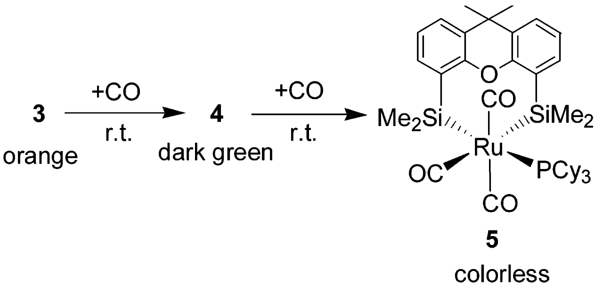


Figure 2. Optimized structures of **3a** (a) and **3b** (b) by the DFT calculation (B3LYP) with the use of the basis set, i.e., SCC for Ru, 6-31G(d) for Si and P, and 6-31G for the rest.

The coordinative unsaturation of **3** was clarified by reaction of **3** with CO. Introduction of CO gas into an NMR tube containing the CD$_2$Cl$_2$ solution of **3** at room temperature caused the solution to turn from orange to dark green and then finally colorless (eq 3). Accordingly, the ^{31}P NMR spectrum indicated the existence of the intermediate **4** (δ 37.6), which subsequently led to the formation of the single product **5** (δ 39.3). The corresponding large-scale experiment allowed the isolation of **5** in 84% yield.



(3)

Recrystallization from CH$_2$Cl$_2$/hexane gave colorless crystals of **5** suitable for X-ray diffraction study (Figure 3). Complex **5** adopts a slightly distorted octahedral geometry in which three carbonyl ligands are located in a *mer*-relationship. The PCy$_3$ ligand occupies the *trans* position of the silyl group (Si1). Unusual stretching of two ruthenium−silicon bonds [Ru−Si1 2.5366(9) Å, Ru−Si2 2.5730(9) Å] is also observed and can be explained similarly to that for **2**. The significant difference in the length of the two ruthenium−silicon bonds is attributable to electronic and/or steric effects: Steric repulsion between one of the Cy groups (C17−C22) and the methyl group (C4) [C4···C17 3.546(5) Å, C4···C22 3.775(5) Å] lengthens the Ru−Si2 bond. Moreover, the strongly electron-releasing PCy$_3$ ligand, located at the *trans* position of the Si1 atom, effectively increases the back-donation from Ru (dπ) to Si1 (σ*),[4] resulting in shortening of the Ru−Si1 bond.

As demonstrated in the reaction of **3** with CO, without regard to the existence of the ruthenium−oxygen bond,

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[4] (a) Eisen, M. S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Chapter 35, p 2037. (b) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; Chapters 9, 10, pp 245, 309.

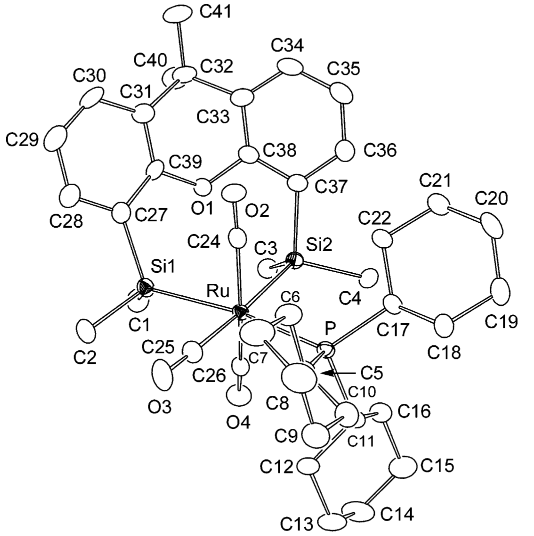

Figure 3. Molecular structure of **5** with thermal ellipsoids at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Ru−Si1 2.5366(9), Ru−Si2 2.5730(9), Ru−P 2.4935(8), C1⋯C3 3.4181(6), C2⋯O3 3.089(5), C4⋯C17 3.546(5), C4⋯C22 3.775(5), P−Ru−Si1 167.93(3), C25−Ru−Si2 175.93(11), C26−Ru−C24 159.89(14).

complex **1** could become a synthetic equivalent of the Ru(II) species with 14 valence electrons.[5] Such 14-electron species are expected to exhibit higher catalytic activity than the corresponding 16-electron species[6] through the presence of two easily accessible, low-lying empty orbitals that can be used in reactions involving successive binding of substrates, oxidative addition, or migration, etc. The catalytic activity of **3** is therefore of great interest.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research (Nos. 14204065, 14044010, and 14078202) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. One of authors (M.O.) wishes to thank the Nissan Science Foundation, the Inoue Foundation for Science, and the Tokuyama Science Foundation.

Supporting Information Available: Experimental details of the synthesis and characterization of all compounds and theoretical study of **3** (PDF), and full details of the X-ray diffraction study in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[5] (a) Ogasawara, M.; Huang, D.; Streib, W. E.; Huffman, J. C.; Gallego-Planas, N.; Maseras, F.; Eisenstein, O.; Caulton, K. G.; *J. Am. Chem. Soc.* **1997**, *119*, 8642. (b) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087. (c) Huang, D.; Bollinger, J. C.; Streib, W. E.; Folting, K.; Young, V., Jr.; Eisenstein, O.; Caulton, K. G. *Organometallics* **2000**, *19*, 2281. (d) Watson, L. A.; Ozerov, O. V.; Pink, M.; Caulton, K. G. *J. Am. Chem. Soc.* **2003**, *125*, 8426.

[6] Crabtree, R. H. In *Activation and Functionalization of Methane*; Davies, J. A., Ed.; VCH: New York, 1990; p 69.