ca. 2 h to a cooled (0 °C) and stirred solution of hexamethyldisilazane (20 mL, 95 mmol) in 100 mL of diethyl ether. After stirring at 20 °C for ca. 2 h, the white crystals were filtered off, washed with cooled *n*-hexane, dried in vacuo, and recrystallized from cold OEt_2–*n*-C_6H_{14} to afford the analytically pure, air-sensitive compound (**1**).

In another preparation, *n*-butyllithium (37 mL of a 1.6 M solution in *n*-C_6H_{14}, 59.2 mmol) was added dropwise during ca. $^1/_2$ h to a stirred solution of 2,2,6,6-tetramethylpiperidine (10 mL, 59.4 mmol) in *n*-C_5H_{12} (40 mL). The reaction mixture slowly became opalescent, and after stirring overnight, a white precipitate and pale yellow solution was observed. The mixture was filtered, and the white solid was washed with cold (0 °C) *n*-pentane and pumped dry to give the very air-sensitive, slightly pyrophoric, crystals of analytically pure compound (**2**).

Acknowledgment. We are grateful to SERC for the award of a studentship to M.J.S. and a fellowship to A.S. and to the National Science Foundation for partial support (to J.L.A.).

Registry No. 1, 84040-90-4; **2**, 84040-91-5.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, and observed and calculated structure factor amplitudes for **1** and **2** (19 pages). Ordering information is given on any current masthead page.

Silane Surface Chemistry of Palladium: Synthesis of Silaethylene, Silacyclobutadiene, and Silabenzene

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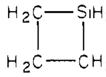
Chemisorption of cycloalkenes on metal surfaces are followed by dehydrogenation processes[1] that often give chemisorbed C_nH_n species, e.g., cyclohexene → benzene[1-3] and cyclooctadiene → cyclooctatetraene.[1] Because these transformations are facile, we have been exploring the reactions of organosilanes with single-crystal metal surfaces[4] as routes to compounds in which there are Si–C bonds of multiple bond order. With platinum and nickel, we observed either no dehydrogenation or gross degradation of the silaalkane.[5] Palladium, however, has furnished dehydrogenation syntheses of silaethylenes, silabenzene, and what appears to be silacyclobutadiene.[6]

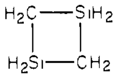
Tetramethylsilane on Pd(110) desorbed fully and intact at $\sim$–50 °C analogous to neopentane on Pd(110), which quantitatively desorbed with a T_{max} of $\sim$–60 °C. In sharp contrast, trimethylsilane after adsorption at –135 °C underwent two competing thermal processes: (i) reversible desorption with a maximum desorption rate at –20 °C; (ii) dehydrogenation to form $(CH_3)_2Si{=}CH_2$,[8,9] which desorbed with maximum rates at –40 and +90 °C (the surface was essentially free of Si and C after the desorption experiment). The latter process was accompanied by H_2 desorption, which also exhibited maxima at –40 and +90 °C. Minor dimerization of the silaethylene also occurred: $[-Si(CH_3)_2CH_2-]_2$ desorbed to give a broad peak at $\sim$40 °C. An unexpected feature here was desorption of silaethylene because most alkenes and alkynes *irreversibly* chemisorb on clean transition-metal surfaces. Consistent with the organosilane surface chemistry, we have found that acetylene and ethylene chemisorb on Pd(110) in a partially reversible fashion.[10]

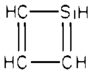
Displacement of the silaethylene, $(CH_3)_2Si{=}CH_2$, from the Pd(110) surface was effected with $P(CH_3)_3$. On dosing the crystal face with $P(CH_3)_3$ at +25 °C, there was immediate displacement of the silaethylene, the dimer, $[-Si(CH_3)_2CH_2-]_2$, and trimethylsilane.

The silaethylene $(CH_3)_2Si{=}CH_2$ was also produced in the thermal desorption experiments with $(CH_3)_3SiOSi(CH_3)_3$, $(CH_3)_3SiNHSi(CH_3)_3$, and $(CH_3)_3SiN_3$ on Pd(110). All three also exhibited partially reversible chemisorption. In the azide system, an additional and major product was $[-(CH_3)_2SiN(CH_3)-]_2$.

Silacyclobutane displayed a complex Pd(110) surface chemistry. After adsorption at –135 °C, silanes **1**–**4** were observed in the


1


2


3

$H_2Si{=}CH_2$
4

thermal desorption with respective desorption maxima at $\sim$–65, +65, +50, and +70 °C, respectively. Ethylene and hydrogen were observed with similar T_{max} of 60–80 °C. All these species were observed in a chemical displacement reaction with $P(CH_3)_3$. Silacyclobutadiene is a new compound, and its characterization must be considered tentative in that it is based solely on mass spectrometric data. The parent ion was less intense than the parent-minus-one ion, as expected for a species with one Si–H bond. Ostensibly, silaethylene[9c] was the precursor to the dimer **2**. Consistent with this presumption, the ratio of **4** to **2** increased when the heating rate was increased from 25 to 75 °C s^{-1}.

Silacyclohexane, initially adsorbed on Pd(110) at –135 °C, also underwent two competing surface reactions: reversible desorption (T_{max} = –25 °C) and dehydrogenation to give silabenzene,[12] SiC_5H_6 (two T_{max} of 90 and 190 °C), and H_2 (two T_{max} of 15 and 190 °C). This chemistry parallels that of cyclohexene, which gave benzene with a T_{max} (C_6H_6) of 220 °C and also of piperidine, which gave pyridine with T_{max} (NC_5H_5) of 115 and 155 °C.[10] Silabenzene was not displaced by $P(CH_3)_3$ from the surface generated from silacyclohexane at temperatures of 25–70 °C.

There are a number of remarkable features to this Pd(110) chemistry. One is the extensive degree of reversible chemisorption of unsaturated hydrocarbons like acetylene, ethylene, and of course, silaethylene and silabenzene. Secondly, these results suggest a practical synthesis of silaethylenes, silacyclobutadienes, and silabenzenes by palladium-catalyzed dehydrogenation of organosilanes, an aspect now under study in our laboratories.[13,14] Also,

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(1) Tsai, M.-C.; Stein, J.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 3533–3534.

(2) Gates, B. C.; Katzer, J. R.; Schuitt, G. C. A. "Chemistry of Catalytic Processes"; McGraw Hill: New York, 1979; pp 222–247.

(3) (a) Tsai, M.-C.; Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2539–2543. (b) Tsai, M.-C.; Muetterties, E. L. *J. Phys. Chem.* **1982**, *86*, 5067.

(4) See references in ref 3 for the equipment, techniques, and procedures for these ultrahigh vacuum experiments. Adsorption was generally effected at –135 °C, and desorption studies were usually done with 25 °C s^{-1} heating rates.

(5) Tsai, M.-C.; Friend, C. M.; Johnson, A. L.; Muetterties, E. L., unpublished data.

(6) The contrasting behavior of palladium with respect to platinum might be traced to a uniquely low Pd–Si bond energy.[7]

(7) Auwiera-Matieu, A. V.; Peeters, R.; McIntyre, N. S.; Drowart, J. *Trans. Faraday Soc.* **1970**, *66*, 809–816.

(8) This compound was characterized only by its mass spectrum. The essential absence of a parent-minus-one ion clearly indicated that this species contained no Si–H bond. This silaethylene molecule has been prepared by thermolysis of tetramethylsilane and trimethylsilane.[9] The alternative formulation of such species as silylenes is critically reviewed by Schaefer.[9c]

(9) (a) Fritz, G.; Grobe, J.; Kummer, D. *Adv. Inorg. Radiochem.* **1965**, *7*, 364. (b) Davidson, I. M. T.; Lamberty, C. A. *J. Chem. Soc. A* **1977**, 882. (c) Schaefer, H. F., III *Acc. Chem. Res.* **1982**, *15*, 283–290.

(10) Gentle, T. M.; Muetterties, E. L., to be published.

(11) References to the generation by thermal processes, mass spectrum, and trapping of silabenzene are given in ref 12.

(12) (a) Solouk, B.; Rosmus, P.; Bock, H.; Maier, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 51. (b) Barton, T. J.; Burns, G. T. *J. Am. Chem. Soc.* **1978**, *100*, 5246.

(13) Since compounds with Si–C multiple bonds readily dimerize or polymerize, the ultrahigh vacuum reaction conditions are ideal for observation of such compounds. However, this technique is impractical for the generation of sufficient quantities for chemical trapping experiments. We plan to examine Pd-catalyzed organosilane dehydrogenation reactions under flow conditions by using very short contact times and matrix or chemical trapping conditions.

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this technique of metal-catalyzed dehydrogenation of readily available, saturated organometallic compounds should provide a useful route not only to new compounds with multiple bonds to silicon[13] but also to new very reactive monomers with multiple bonds based on other elements such as P, Ge, Al, etc. Third, we note that the saturated organosilanes in which there is at least one Si–H bond are far more susceptible to dehydrogenation than are saturated hydrocarbons; for example, cyclohexane and tetramethylsilane undergo fully reversible chemisorption on Pd(110) under ultrahigh vacuum conditions, in contrast to silacyclohexane and trimethylsilane. Apparently, a primary surface interaction of Si–H species is through a three-center $\equiv$Si—H—M_{surf} bond: note the substantially higher desorption temperature for $(CH_3)_3SiH$ (T = −20 °C) than for $(CH_3)_4Si$ (T = −50 °C).

Acknowledgment. This work was supported by the National Science Foundation, by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, and by a grant from the Dow Chemical Co. T.M.G. also thanks the Dow Corning Corp. for a grant in the form of a graduate fellowship. We also thank Professor Thomas Barton for the sample of monosilacyclobutane and Dr. Maher Elsheikh for the trimethylsilane and silacyclohexane.

Registry No. 1, 287-29-6; **2**, 287-55-8; **3**, 76893-79-3; **4**, 51067-84-6; $(CH_3)_3SiH$, 993-07-7; $(CH_3)_2Si{=}CH_2$, 4112-23-6; H_2, 1333-74-0; $[Si(CH_3)_2CH_2]_2$, 1627-98-1; $(CH_3)_3SiOSi(CH_3)_3$, 107-46-0; $(CH_3)_3SiNHSi(CH_3)_3$, 999-97-3; $(CH_3)_3SiN_3$, 4648-54-8; $[(CH_3)_2SiN(CH_3)]_2$, 1073-92-3; SiC_5H_6, 289-77-0; Pd, 7440-05-3; silacyclohexane, 6576-79-0.

Supplementary Material Available: Thermal desorption spectra for Pd(110)–trimethylsilane, Pd(110)–silacyclobutane, and Pd(110)–silacyclohexane (6 pages). Ordering information is given on any current masthead page.

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(14) The Pd(100) surface has an organosilane chemistry analogous to that of Pd(110).

Cationic η^2-Arene Complexes of Rhenium in Carbon–Hydrogen Bond Activation

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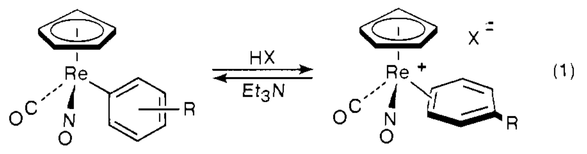
Few η^2–arene complexes of transition metals have been characterized,[1] but they have long been considered to be plausible intermediates in the activation of aromatic carbon–hydrogen bonds.[2] We now report a generally applicable synthesis of η^2-arene complexes of the $[(\eta\text{-}C_5H_5)Re(NO)(CO)]^+$ cation[3] and observations on them that suggest a striking correspondence with the intermediates of electrophilic aromatic substitution.

Table I

complex	R	molar ratio	
		para	meta
3b	CH_3	94	6
1[3]	$CHPh_2$	55	45
3c	CF_3	16	84

The method involves protonation of the appropriate aryl derivative[4] at low temperature in dichloromethane (eq 1).[5] Thus



(1)

2a R = H
2b R = CH_3
2c R = CF_3

3a R = H, X = BF_4
3b R = CH_3, X = BF_4
3c R = CF_3, X = SO_3F

addition of $HBF_4{\cdot}Et_2O$ to **2a** in CH_2Cl_2 at −78 °C precipitated **3a** as a yellow solid isolated at low temperature.[6] Formulation as the η^2-benzene cation **3a** is based on reactions and spectroscopic observations made in CH_2Cl_2 solution between −50 and −90 °C.[7] Noteworthy is the singlet for the η-C_6H_6 ligand at δ 7.23, which was not affected by addition of a small amount of benzene; an additional singlet due to free benzene appeared at δ 7.33. Coordinated benzene therefore does not dissociate at a significant rate on the NMR time scale, and the δ 7.23 singlet is the result of a fluxional process in **3a**.

Similar low-temperature protonations of the ortho, meta, or para isomers of **2b** (with use of $HBF_4{\cdot}OEt_2$) led *in each case* to the same product, a yellow solid characterized as the η^2-toluene cation **3b**.[9] The ^1H NMR spectrum exhibits five nonequivalent protons in the aromatic region.[9] As argued in detail for **1**,[3] this is consistent with migration of the rhenium group from one η^2 position to another via η^1-arenium intermediates such as **4b**.[10] Such a migration would account for the fluxionality of **3a**.

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(1) (a) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. *Chem. Rev.*, in press. (b) Browning, J.; Green, M.; Penfold, B. R.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1973**, 31. (c) Cobbledick, R. E.; Einstein, F. W. B. *Acta Crystallogr., Sect. B* 1978, *B34*, 1849. We exclude arene complexes of d^{10} metals from consideration here.

(2) (a) Parshall, G. W. *Catalysis* (*London*) **1977**, *1*, 335. (b) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; Chapter 7. (c) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 325. (d) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240.

(3) We have reported a specific preparation of the triphenylmethane complex $[(\eta\text{-}C_5H_5)Re(NO)(CO)(3,4\text{-}\eta^2\text{-}Ph_3CH)](PF_6)$ (**1**) by utilizing the reaction of $[Ph_3C][PF_6]$ with $(\eta\text{-}C_5H_5)Re(NO)(CO)H$: Sweet, J. R.; Graham, W. A. G. *Organometallics*, in press.

(4) The required aryl derivatives (**2a**; *o*-, *m*-, and *p*-**2b**; *m*- and *p*-**2c**) have been prepared in high yield by using organocopper reagents: Sweet, J. R.; Graham, W. A. G. *J. Organomet. Chem.*, in press.

(5) Complexes **3** are drawn for convience with fully localized double bonds. Realistic discussion of bonding will require a crystallographic study, and we are seeking derivatives of sufficient stability to permit this.

(6) The lifetime of solid **3a** at room temperature is substantially shorter than that of **1**,[3] and an analysis was not obtained. As in the case of **1**, decomposition of CH_2Cl_2 solutions of **3a** became rapid above ca. -40 °C.

(7) Properties of **3a**: (a) Reaction at −78 °C with PPh_3 formed benzene and the known[3,8] cation $[(\eta\text{-}C_5H_5)Re(NO)(CO)(PPh_3)]^+$ in high yield. (b) Reaction of isolated **3a** at −78 °C with Et_3N (eq 1) regenerated **2a** in 92% yield. (c) IR (CH_2Cl_2) 2015 (ν_{CO}), 1760 cm^{-1} (ν_{NO}). (d) ^1H NMR $(CD_2Cl_2$, −50 to −90 °C) δ 6.19 (s, 5 H, C_5H_5), 7.23 (s, 6 H, η^2-C_6H_6).

(8) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.

(9) Properties of **3b**: similar thermal stability to **3a**; reacts with Ph_3P to displace toluene; IR (CH_2Cl_2) 2015 (ν_{CO}), 1760 cm^{-1} (ν_{CO}). ^1H NMR (400 MHz, CD_2Cl_2, −60 °C) δ 2.52 (s, 3 H, CH_3), 6.18 (s, 5 H, η-C_5H_5), 6.91 (d, 1 H), 7.02 (m, 2 H), 7.08 (t, 1 H), 7.20 (t, 1 H); decoupling experiments suggest that the δ 7.02 multiplet results from the near coincidence of a doublet and a triplet due to two different protons. The NMR spectrum is available as supplementary material.

(10) Briefly, failure to observe the diastereomers expected for a static structure **3b** requires their rapid interconversion. Further, in intermediate **4b**, a diastereotropic relationship is imposed on opposite edges of the ring by the chiral rhenium group. The five aromatic protons are thus nonequivalent in all static structures, and the time-averaged spectrum would show five nonequivalent protons (barring accidental degeneracies). Only the para form of the η^1-arenium ions is shown, but meta forms are postulated as well in view of the deprotonation results (vide infra).

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