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 ≡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).

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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.

(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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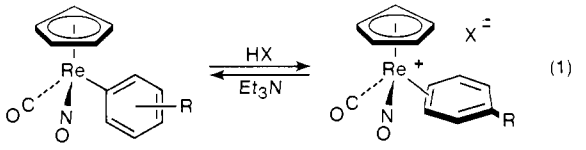
Few η^2–arene complexes of transition metals have been characterized,[1] but they have long been considered to be plausible intermediates in the activation of aromatic carbon–hydrogen bonds.[2] We now report a generally applicable synthesis of η^2-arene complexes of the $[(\eta\text{-}C_5H_5)Re(NO)(CO)]^+$ 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	molar ratio 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**.

(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.

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(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).

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(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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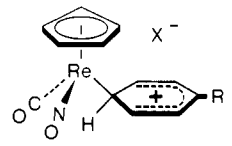

4a R = H, X = BF_4
4b R = CH_3, X = BF_4
4c R = CF_3, X = SO_3F

Protonation of the trifluoromethyl derivatives *m*-**2c** and *p*-**2c** at −78 °C required fluorosulfonic acid.[11] Both isomers afforded the same salt, **3c**, as an intractable oil that could not be isolated in the manner of **3a** and **3b**. Spectra of good quality were nevertheless obtained.[12]

Further evidence consistent with an equilibrium between the η^2-forms **3** and small amounts of the η^1-arenium species **4** is now provided by deprotonation studies. Complexes **3b** and **3c**, as well as **1**,[3] are deprotonated by triethylamine in high yield at −78 °C (the reverse of eq 1). In each case the products of deprotonation are the para and meta aryls, in a ratio dependent upon the ring substituent as summarized in Table I.

A clear trend toward an increased para:meta ratio as the electron-releasing ability of the substituent increases is apparent. Apart from the lack of detectable ortho aryl isomers, this trend parallels the directive effects of electrophilic aromatic substitution and can be similarly explained by familar arguments[13] as to the relative stabilities of the para and meta η^1-arenium cations through which deprotonation of the η^2-arene cations is believed to occur.

These direct observations of η^2-arene complexes add substance to earlier suggestions as to their role as intermediates.[2] Not surprisingly, the properties of the η^2-arene cations differ markedly from those of related η^2-olefin compounds.[14] The present work provides evidence for a mechanism of aromatic carbon–hydrogen activation by $[(\eta\text{-}C_5H_5)Re(NO)(CO)]^+$ that may be common to many cationic, electrophilic metal centers.[2a,b] However, carbon–hydrogen activation by metal centers having different electronic properties will in all likelihood follow different pathways; recent examples of activation by an oxidative-addition process are provided by the relatively electron-rich intermediates $(\eta\text{-}C_5Me_5)Ir(PMe_3)$[15] and $(\eta\text{-}C_5Me_5)Ir(CO)$.[16]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council and the University of Alberta for financial support.

Registry No. 2a, 84081-68-5; **2b** (R = *o*-CH_3), 84081-69-6; **2b** (R = *m*-CH_3), 84081-70-9; **2b** (R = *p*-CH_3), 84081-71-0; **2c** (R = *m*-CH_3), 84081-72-1; **2c** (R = *p*-CH_3), 84081-73-2; **3a**, 84081-75-4; **3b**, 84081-77-6; **3c**, 84081-79-8.

Supplementary Material Available: ^1H NMR spectrum (400 MHz, CD_2Cl_2, −60 °C) of $[(\eta\text{-}C_5H_5)Re(NO)(CO)(3,4\text{-}\eta^2\text{-}C_6H_5CH_3)][BF_4]$ (**3b**) (1 page). Ordering information is given on any current masthead page.

(11) The rate of protonation of *m*- and *p*-**2c** by $HBF_4{\cdot}Et_2O$ was significant only above −60 °C, where decomposition was moderately rapid, giving rise to a ^1H NMR signal at δ 5.99, which we tentatively ascribe to $(\eta\text{-}C_5H_5)Re(NO)(CO)(FBF_3)$. This implies displacement of $\eta^2\text{-}C_6H_5CF_3$ by a fluorine-bonded BF_4^- counterion and demonstrates the extraordinary lability of this η^2-arene ligand. Trifluoromethylsulfonic acid protonates **2c** below −60 °C, but above −80 °C the counterion displaces $C_6H_5CF_3$, forming stable $(\eta\text{-}C_5H_5)Re(NO)(CO)(OSO_2CF_3)$, which we have prepared independently and fully characterized.

(12) Data for **3c**: IR (CH_2Cl_2) 2013 (ν_{CO}), 1757 cm^{-1} (ν_{NO}); ^1H NMR (CD_2Cl_2, −78 °C) δ 6.19 (s, 5 H, C_5H_5), 6.74 (t, 1 H), 7.20 (overlapping triplets, 2 H), 7.31 (d, 1 H), 7.53 (d, 1 H).

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(14) The very stable $[(\eta\text{-}C_5H_5)Re(NO)(CO)(1,2\text{-}\eta^2\text{-}C_7H_8)][BF_4]$ shows no evidence for nonrigidity and does not react with PPh_3 at room temperature: Sweet, J. R.; Graham, W. A. G. *J. Organometal. Chem.* **1981**, *217*, C37.

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Protein Structure by Solid-State NMR

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This communication outlines a general approach for determining the structure of proteins and other biopolymers that are part of supramolecular structures that orient in the applied magnetic field of an NMR spectrometer. The method is illustrated with the Trp-26 side chain of the coat protein of fd bacteriophage. Since the protein is part of an infectious virus particle in solution, this is an in vivo structure determination.

This approach exploits the spectral simplifications that accompany macroscopic uniaxial orientation of a polymeric sample parallel to the magnetic field.[1] The angular dependence of nuclear spin interactions described by second-rank tensors is used to determine the orientation of individual sites relative to the axis of orientation. Solid-state NMR studies of oriented and unoriented samples allows geometrical and dynamical parameters[2] to be explicitly separated and analyzed to give an integrated view of protein structure. A variety of biological structures are oriented by strong magnetic fields, including membrane–protein and nucleoprotein complexes;[3] as higher magnetic fields become available and more suitable conditions are developed, it can be anticipated that many interesting systems will be amenable for structural NMR studies. Myoglobin crystals orient in a magnetic field because of the paramagnetic iron in the heme group; this made possible NMR studies of labeled sites in the protein similar to those described here.[4]

The filamentous bacteriophages are nearly ideal systems for these investigations. Their large size (9 nm by 900 nm) is a result of the symmetrical arrangement of 2700 helical coat protein subunits extended along the filament.[5] Almost all of the carbonyl groups of the peptide linkages are parallel to the filament axis, and their total diamagnetic anisotropy results in essentially perfect alignment of the virus particles in the magnetic field.[6] Each coat protein has a single tryptophan residue (Trp-26), which can be labeled with stable isotopes. Previous NMR studies have shown this residue to be immobile on the slowest time scale measured (10^3 Hz) and to have the same environment in all of the coat protein subunits.[2]

The angular dependence of the nuclear spin interactions is directly manifested in solid-state NMR spectra. In unoriented samples, the resonances are powder patterns, while in oriented samples, the resonances are single lines (chemical shift anisotropy) or doublets (quadrupole, dipole) whose frequencies reflect the relative orientation of the spin interaction tensor and the applied magnetic field. The most general case is where the tensor is completely asymmetric, i.e., none of the principal elements have the same magnitude. The nonaxially symmetric $^{15}N_{\epsilon_1}$ chemical shift anisotropy of tryptophan gives the characteristic powder pattern in Figure 1A. The magnitudes of the principal values of the chemical shift tensor are determined from the discontinuities of the powder pattern. The orientations of the principal axes in the molecular frame shown in Figure 1 are based on those found for secondary amines, including histidine,[7] where σ_{33} is along the N–H bond axis and σ_{11} is perpendicular to the plane of the C–N

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