of solvents, the *bis*-silyl alcohol 10 (with purity $>$ 95 % by TLC and NMR) was obtained in 72 % yield[4]; TLC R_f 0.44 (50 % ether/hexane) (Scheme).

In summary, herein is reported a methodology by which C-3 functionalization on thiophene rings is cleanly achieved by means of C-5 protection with a silyl group (which is a super proton equivalent)[7,8] and of *ortho*-metalation utilizing an existing anchoring group at C-2. In view of recent brillant progress in organosilane chemistry[7,8], one should be able to transform the silicon-bearing carbons into nucleophiles or electrophiles, as well as its parent methine carbons. Extension of this concept and data refinement are under vigovous progress.

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The yields herein are not optimized, and the nmr spectral data for some selected compounds are summarized (CCl_4, $CHCl_3$ reference):

3,   7.0~7.4(m, 3H), 0.30 (s, 9H); 4,   6.9 (m, 2H), 4.9(q, 1H), 1.46(d, 3H), 0.23(s, 9H); 6,   6.83(s, 1H), 4.96(q, 1H), 2.13(s, 3H), 1.43(d, 3H), 0.23(s, 9H); 7, 6.8-7.2(m, 3H), 4.9 (q, 1H), 1.43(d, 3H); 8, 6.8(m, 2H), 4.96 (g, 1H), 1.41(d, 3H), 0.60(s, 9H), 0.26(s, 9H); 4.96(q, 1H), 1.41(d, 3H), 0.60(s, 9H), 0.26(s, 9H); 10, 6.96(s, 1H), 5.1(q, 1H), 1.4(d, 3H), 1.4(d, 3H), 0.16(s, 18H).

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A Simple Proton NMR Spectrum of Coordinated Acrylonitrile

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We wish to report a simple 8-line proton NMR spectrum for coordinated acrylonitrile in $[Rh(CH_2=CHCN)(CO)(P(C_6H_5)_3)_2]ClO_4$[1] where $CH_2=CHCN$ is coordinated through nitrogen[2] (free acrylonitrile gives rise to a complex 13-line ABC pattern). There have been two reports giving detailed proton NMR spectral data for coordinated acrylonitrile through nitrogen to transition metals.[4,5] It was found that the proton NMR spectra of coordinated acrylonitrile (in $[Ru(NH_3)_5(CH_2=CHCN)]^{2+}$ and $[Rh(NH_3)_5(CH_2=CHCN)]^{3+}$,[4] and $W(CO)_4(CH_2=CHCN)_2$[5]) are essentially identical with that of free acrylonitrile except that the chemical shifts are slightly shifted and the coupling constants show small changes. Accordingly, computer refinements were necessary to obtain the spectral parameters in both studies.[4,5]

Figure 1 is proton NMR spectrum of $[Rh(CH_2=CHCN)(CO)(P(C_6H_5)_3)_2]ClO_4$ which we recently prepared.[1] There are only 8 peaks attributable to the coordinated acrylonitrile in the region of 5.0~7.0 ppm (relative to TMS) in Figure 1, whereas free acrylonitrile shows a complex ABC pattern
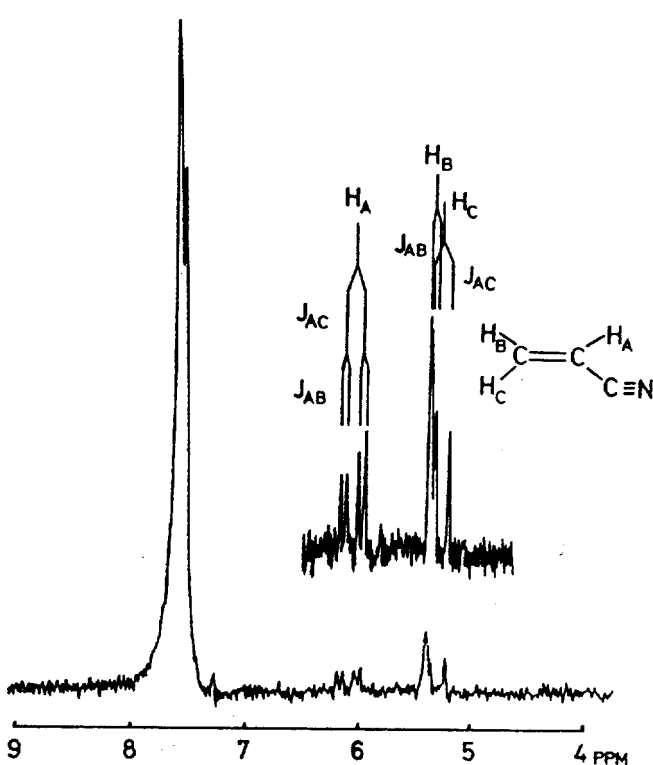
centered at *ca.* 6.0 ppm.[6] It is easily seen in Figure 1 that the doublet of doublet at 6.05 ppm is due to H(A) coupled by H(B) and H(C). The coupling constants, $J(AB)$ and $J(AC)$ are clearly confirmed by the two doublets at 5.35 ppm due to H(C) and at 5.47 ppm due to H(B), respectively, whereas the coupling between the geminal protons, H(B) and H(C) is not observed. No evidence is obtained for the coupling due to ^{103}Rh or ^{31}P.

Table 1 summarizes the spectral data for free $CH_2=CHCN$ and $CH_2=CHCN$ in $[Rh(CH_2=CHCN)(CO)(P(C_6H_5)_3)_2]ClO_4$. The small downfield shift (+0.31 ppm) for H(A) observed in this study lies within the range of the downfield shifts (+0.13~0.40 ppm) reported for the acrylonitrile coordinated through nitrogen in the previous studies.[4,5] The changes in the chemical shifts of H(B) and H(C) due to the coordination through nitrogen have been reported to be either way (upfield shift: -0.27 ppm for H(B) and -0.16 ppm for H(C) in Ru(II) complex,[4] and downfield shift: +0.37 ppm for H(B) and +0.43 ppm for H(C) in Rh (III)

complex[4]) or practically not at all (−0.03 ppm for H(B) and −0.04 ppm for H(C) in W(O) complex[5]). The upfield shifts observed in this study, −0.66 ppm for H(B) and −0.92 ppm for H(C) are relatively large, which may be understood in terms of electron richness of Rh(I) in this study.

The changes in the coupling constants of acrylonitrile that result from coordination are striking in this study (see Table 1), whereas only small changes were observed in the previous two studies[4,5] where J(AB)=10.5∼12.2 Hz, J(AC)= 16.8∼17.9 Hz and J(BC)=0.2∼0.9 Hz were obtained. **Figure 1.** Proton NMR spectrum of [Rh($CH_2=CHCN$)-(CO) (P(C_6H_5)$_3$)$_2$] ClO_4 in $CDCl_3$ at 25 °C. The small peak at 7.27 ppm (relative to TMS) is due to residual $CHCl_3$.

These significant changes in coupling constants and in chemical shifts of H(B) and H(C) observed in this study convert the complex 13-line ABC pattern spectrum of free acrylonitrile into the simple 8-line spectrum of acrylonitrile in [Rh($CH_2=CHCN$)(CO)(P(C_6H_5)$_3$)$_2$]ClO_4 as seen in Figure 1.

Experimental

[Rh($CH_2=CHCN$)(CO)(P(C_6H_5)$_3$)$_2$]ClO_4 was prepared by the literature method.[1] Proton NMR spectrum was recorded on a 60 MHz spectrometer (Varian Model EM–360A) under nitrogen at 25 °C.

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