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6e in 52-85% yield.

A stereochemical assignment (*syn/anti*) for the resulting *N*-coupled products could be established through the chemical shift of the C-3-methine proton of the piperazine-2,5-dione ring. It was reported that the C-3 methine protons appear as a sharp singlet for the *syn*-bis(sulfide) while the *anti* diastereomer exhibited C-3 methine protons as two singlets in the symmetrically α-*S*-functionalized piperazine-2,5-dione and this relationship was also derived from the single-crystal X-ray analysis.[6] Our results also shows that *N*-substituted C-3 methine protons give one sharp singlet peak as a major peak at 4.16, 4.21 or 6.49 ppm (**6d**). Although X-ray analysis is needed to determine the exact stereochemistry, we believe that the products we have prepared are of *syn* stereochemistry as these have been shown to be thermodynamically more stable by previous authors.[6]

Substituent (R)	C-3 methine	yield(%)	mp.
piperidine (**6a**)	4.16 ppm	79.0	181-182
pyrrolidine (**6b**)	4.21 ppm	52.0	230(dec.)
N-methylpiperidine (**6c**)	4.21 ppm	71.8	178-180(dec.)
imidazole (**6d**)	6.49 ppm	84.6	239(dec.)
morpholine (**6e**)	4.21 ppm	83.5	150-151

In conclusion, the methodology outlined above, describes a practical approach to α-*N*-functionalized piperazine-2,5-diones. The stereochemical assignment (*syn/anti*) is currently under investigation and will be reported in the full paper.

A typical experimental procedure is as follows. To a stirred suspension of NaH (0.12 g, 4.1 mmol, 2.2 equiv. 80% in oil) in 5 mL THF was added piperidine (0.352 g, 4.1 mmol, 2.2 equiv.) slowly under argon atmosphere. The mixture was stirred for 30 min at room temperature and transferred *via* a syringe into a stirred solution of dibromide, **5**, (0.85 g, 1.9 mmol) in 12 mL THF. The mixture was allowed to stir for 30 min and poured into water and extracted three times with $CHCl_3$. The combined organic extracts were dried ($MgSO_4$), filtered, and purified by column chromatography (SiO_2, 7 : 1, hexane/ethyl acetate, $R_f=0.55$). 1,4-dibenzyl-3,6-bis(piperidyl)-piperazine-2,5-dione, **6a** was obtained as a white solid (0.68 g, 79%); mp. 181-182°C ; ^{1}H-NMR (300 MHz, $CDCl_3$): 7.3-7.2 (10H, m), 5.4-5.2 (2H, d), 4.31-4.14 (2H, d), 4.16 (2H, s), 2.9-2.6 (4H, m), 2.5-2.3 (4H, m), and 1.8-1.3 ppm (12H, m); IR (KBr): 3200, 2910, 1680, 1450, and 1150 cm^{-1}; Mass spectrum (m/z, rel. intensity): 460 (M$^+$), 376 (7), 375 (34), 292 (42), 91 (100), and 84 (87).

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Infrared Spectrum of Sodium-Benzene Complex in Argon Matrix

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By cocondensing lithium and sodium atoms with benzene diluted in argon, Manceron and Andrews[1] observed new infrared absorptions attributable to mono- and dibenzene complexes in the case of lithium but nothing with sodium. Based on the UV/VIS spectrum of diluted dispersions of sodium atoms in solid benzene, McCullough and Duley[2] suggested, on the other hand, that Na atoms in benzene interacted predominantly with one nearby benzene molecule. Its presence has been proposed also by Moore *et al.*[3] in their electronic absorption study on dilute thin-film codeposits of potassium or rubidium with benzene.

Considering that the physicochemical properties of alkali metals are generally much the same as one another, the interaction behavior of Na to certain molecules may be expected somewhat similar to that of other alkali metals. In fact, Kunze *et al.*[4] found the sodium and potassium atoms to interact with UF_4 similarly to the case of lithium. Based on the above informations, it is conjectured that the sodium-benzene complex can be formed even though its interaction strength is not substantial. In this respect, we are currently investigating the possibility of sodium-arene complex formation by using the matrix isolation infrared spectroscopy. In this report, we wish to present the preliminary observation made on the sodium-benzene system in argon matrix.

The reagent grade benzene and the matrix gas (Ar) were mixed in mole ratios varying from 1 : 70 to 1 : 1000 using a standard manometric technique. The gas mixture was sprayed onto a cold CsI window held at 9 K. Sodium metal atoms, prepared by evaporating natural sodium metal inside the deposition line, was also introduced into the cryostat together with C_6H_6. The sodium concentration was modified by varying the temperature of evaporator, resulting in a 10-fold change in metal pressure. The highest relative proportion of Na and C_6H_6 used here is estimated at 1 : 6.

Experimental setup is nearly the same as that reported previously.[5] A Janis Model 22 closed cycle helium cryocooler was used to cool the CsI substrate down to 9 K. Appropriate
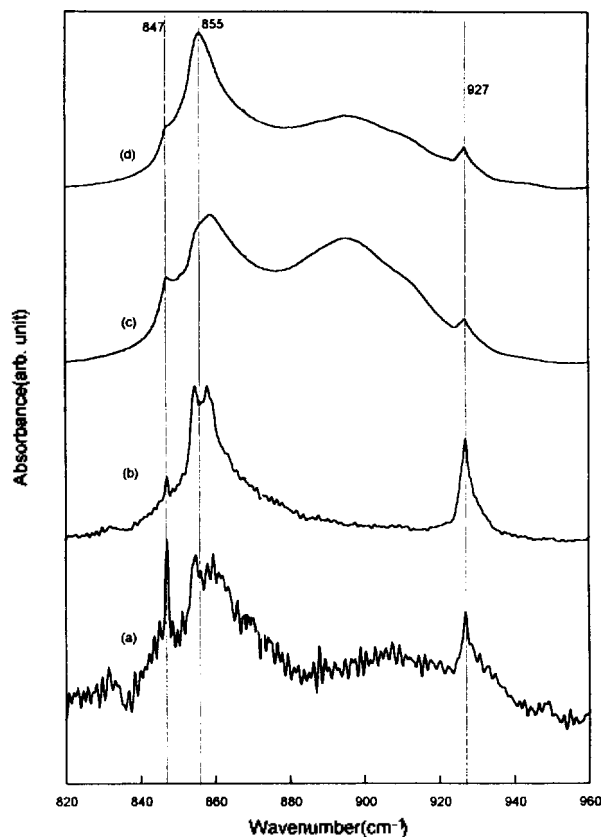
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Figure 1. Infrared spectra in the 820-960 cm⁻¹ region for sodium atoms deposited with mixtures of benzene and Ar on CsI at 9 K, at the Na : C_6H_6 : Ar ratio of (a) 1 : 500 : 500000, (b) 1 : 6 : 6000, (c) 1 : 7000 : 500000, and (d) 1 : 86 : 6000.

Figure 2. Infrared spectra in the 820-960 cm⁻¹ region after annealing at 33 K for 20 minutes for sodium atoms deposited initially with mixtures of benzene and Ar on CsI at 9 K, at the Na : C_6H_6 : Ar ratio of (a) 1 : 500 : 500000, (b) 1 : 6 : 6000, (c) 1 : 7000 : 500000, and (d) 1 : 86 : 6000.

temperature was maintained using the Lake Shore DRC-80-M temperature controller. The pressure of the cryostat, monitored with a Leybold Penningvac PM 310 gauge, was kept below 10^{-5} mbar. Transmission infrared spectra were recorded by using a vacuum-purged Fourier transform infrared spectrometer (Bruker Model IFS 113v) at spectral resolution of 1.0 cm⁻¹. The 1024 times scanned interferograms with a liquid nitrogen cooled MCT (Mercury Cadmium Telluride) detector were averaged for an individual spectrum. The single beam spectrum of the bare cold CsI window was taken as the reference spectrum.

Initially, we have examined the infrared spectrum of benzene alone in argon matrix. The spectra obtained as a function of Ar/C_6H_6 ratio were confirmed to correlate well with those in the literature.[6,7] When sodium was codeposited with benzene, the infrared spectral pattern appeared at the first glance hardly different from that obtained with benzene alone. A closer examination indicated, however, a subtle spectral difference to exist in the 820-960 cm⁻¹ region. From the spectral changes induced by the variation of the metal and benzene concentrations, the bands in the above region were supposed to arise from the interaction species between sodium and benzene.

Figure 1 shows the infrared spectra in the 820-960 cm⁻¹ region for sodium atoms deposited with benzene. It has to be mentioned here that there is no peak in that region in the absence of sodium. At the highest dilution (Na : C_6H_6 :
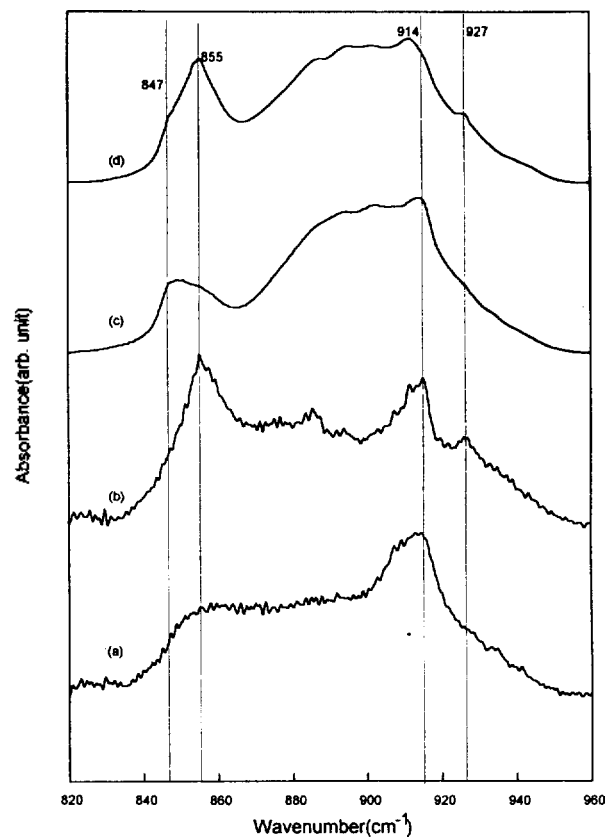
Ar = 1 : 500 : 500000), at least four peaks are identifiable in the region, namely, at 847, 855, 859, and 927 cm⁻¹ as can be seen from Figure 1(a). As the concentration of sodium was increased up to Na : C_6H_6 = 1 : 6, the intensity of the peak centered at 847 cm⁻¹ decreased substantially while the intensities of other peaks were slightly enhanced, as can be seen in Figure 1(b). Besides, the intensities of the bands at 855 and 859 cm⁻¹ were less affected in a relative sense.

As the concentration of benzene was increased, a very broad featureless band appeared around 895 cm⁻¹ (see Figure 1(c) and (d)). This band became more prominent when the benzene/sodium ratio was higher. On the other hand, the relative intensity of the peak at 847 cm⁻¹ diminished concurrently in a fair amount, but the variation of that at 927 cm⁻¹ was less significant. At higher benzene concentration, the peak near 855 cm⁻¹ became intensified upon the concomitant increase of sodium concentration, as can be seen by comparing the spectra shown in Figure 1(c) and (d).

Upon annealing to 33 K for 20 minutes, a new peak centered near 914 cm⁻¹ appeared distinctly irrespective of benzene/sodium ratio, as can be seen from Figure 2. It is also seen that the peak around 855 cm⁻¹ becomes more prominent as the sodium concentration increases (see Figure 2(b) and (d)).

The exact nature of the species responsible for the peaks appearing in Figure 1 is uncertain at the moment. Referring

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to the marked concentration dependence, the peaks appearing in the 820-960 cm^{-1} region may be differentiated into three different kinds of species, namely Na$_x$(C$_6$H$_6$), with $x>y$ (species 1), $x=y$ (species 2), and $x<y$ (species 3). One could assume that the peak being intensified along with the increase of sodium concentration, at a certain benzene concentration, is due to 'species 1'. Based on this, the 927 cm^{-1} peak could be attributed to 'species 1'. The relative invariance of the 927 cm^{-1} peak in the spectra of Figure 1(c) and (d) may be rationalized by assuming that the increase of sodium at higher benzene concentration does not affect greatly the amount of 'species 1'. On the other hand, one could assume that the peak being intensified at higher benzene concentration is due to 'species 3'. Based on this, the peaks appearing around 847, 895, and 914 cm^{-1} could be attributed to 'species 3'. Then, the peaks relatively insensitive to the concentration change, such as those around 855-859 cm^{-1} could be rendered to 'species 2'. Invoking further to the assignments made on the Li-C$_6$H$_6$ complexes,[1] it seems possible to render the peaks at 927, 914, and 859 cm^{-1} to Na$_2$(C$_6$H$_6$), Na(C$_6$H$_6$)$_2$, and Na(C$_6$H$_6$), respectively. Although the doublet at 855 and 859 cm^{-1} may be assigned together to 1:1 complex, the fact that the 855 cm^{-1} peak becomes more prominent in the annealed spectra, taken at higher sodium concentration (Figure 2(b) and (d)), suggests that the peak is more likely to arise from a 1:1 complex with 'x' being greater than 2 in Na$_x$(C$_6$H$_6$)$_y$. Assuming that the peaks at 847 and 895 cm^{-1} are together due to Na(C$_6$H$_6$)$_y$, the value of 'y' corresponding to the latter peak may be greater than that of the former since the latter appears distinctly only at a higher benzene concentration (Figure 1(c) and (d)). In addition, referring once again to the work on the Li-C$_6$H$_6$ complexes,[1] the peaks appearing in Figure 1 and 2 seem to be related with the ring breathing modes of appropriate complex species.

It would be worth to mention that even for the 1:1 Li-C$_6$H$_6$ complex, controversial views remain still on the nature of its structure. From an ESR study, Manceron *et al.*[8] claimed the complex to assume a C$_{2v}$ structure. This is in contrast with the approximation made earlier by Manceron and Andrews.[1] Benzene radical was, on the other hand, predicted to possess a D$_{2h}$ symmetry based on the ab initio molecular orbital calculation.[9] In order to resolve above controversy, information on other systems like Na-benzene will be much helpful.

In summary, it has been shown from the matrix isolation infrared spectroscopy that sodium atoms could form complexes with benzene, in contrast with the earlier work. Although the nature of complex species is not certain at the moment, a tentative assignment has been proposed. Further studies are required to characterize the identities of complex species. Accordingly, research is on progress to examine the isotope effect along with ab initio quantum mechanical calculation.

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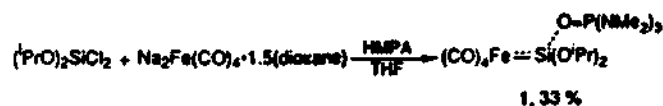9. Hinde, A. L.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1978**, *100*, 4681.

Synthesis, Characterization and Stability of (iPrO)$_2$Si=Fe(CO)$_4$ · HMPA

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Recently, it has been demonstrated that silylene-transition metal complexes are stable as weak donor adducts.[1] Only ten examples of base-stabilized silylene complexes characterized by X-ray diffraction have been reported, and in all cases, coordination of a donor molecule to silicon is observed.[1,2] But little quantitative information on the stability and stereochemistry of these complexes has been published. We report here the synthesis and the characterization of a new donor-stabilized silylene complex, tetracarbonyl(diisopropoxysilanediyl)iron(0)-hexamethylphosphoramide, and the first experimental determination of the free energy of activation for losing stereochemistry at silicon of the donor-stabilized silylene complex.

$$(^iPrO)_2SiCl_2 + Na_2Fe(CO)_4 \cdot 1.5(dioxane) \xrightarrow[THF]{HMPA} (CO)_4Fe = Si(O^iPr)_2 \overset{O-P(NMe_2)_3}{}$$

1, 33 %

The complex was synthesized by employing Collman's reagent, Na$_2$Fe(CO)$_4$, as a metal source in reaction with dichlorodiisopropoxysilane.[1(b),3-5] After recrystallization from diethylether, the compound 1 was obtained as a colorless crystalline complex.[6] It melted at 139-140°C in a sealed capillary without decomposition. The presence of three carbonyl stretching bands (2007, 1926, 1888 cm^{-1}) indicates that the Fe(CO)$_4$ moiety has the local C$_{3v}$ symmetry and the silylene ligand occupies an apical position of trigonal bipyramid config-