

Figure 1. Metal carbonyl infrared stretching frequencies for iron cyanohydrin carbonyl complexes.

In Figure 1 the thick lines in the spectra of complexes 1, 2, and 4 as well as that of $(\text{CO})_4\text{FePF}_3$ represent those $\nu_{\text{C=O}}$ stretches assigned to the axial isomer by using the method of Haas and Sheline.¹³ A calculation of the percent isomer distribution for complexes 1, 2, and 4 gave the following results: $(\text{CO})_4\text{F}_2\text{POC}(\text{CF}_3)_2\text{CN}$, axial 22%, equatorial 78%; $(\text{CO})_4\text{FeF}_2\text{POCNC}_2(\text{CF}_3)_4\text{O}$, axial 40%, equatorial 60%; $(\text{CO})_4\text{FeFP}[\text{OC}(\text{CF}_3)_2\text{CN}]_2$, axial 15%, equatorial 85%. Only complex 4 exhibits a statistical distribution of isomers. Thus it is apparent that, as the degree of substitution of fluorine by the cyanohydrin group $\text{OC}(\text{CF}_3)_2\text{CN}$ increases, the equatorial isomer becomes more favored. This is in contrast with the results of methoxy substitution since $(\text{CO})_4\text{FeP}(\text{OCH}_3)_3$ exists only as the axial isomer whereas $(\text{CO})_4\text{FeP}[\text{O}(\text{CCF}_3)_2\text{CN}]_3$ exists only as the equatorial isomer.

It is tempting to attribute this difference to the difference in steric requirements of the axial and equatorial positions in the TBP arrangement. Since the cone angle of $\text{Po}[\text{OC}(\text{CF}_3)_2\text{CN}]_3$ must be considerably larger (an angle of at least 160°) than that of $\text{P}(\text{OCH}_3)_3$ (107°),⁶ the cyanohydrin derivative would be expected to favor the equatorial position over $\text{P}(\text{OCH}_3)_3$. This would also explain the increasing amount of equatorial isomer formation as cyanohydrin groups are substituted for fluorine as illustrated by complexes 1 and 2.

The importance of electronic effects is not clear, but steric factors alone can not explain why triphenylphosphine forms only the axial isomer⁵ while $\text{F}_2\text{POC}(\text{CF}_3)_2\text{CN}$ forms predominantly the equatorial isomer. A comparison of the $\nu_{\text{C=O}}$ stretching frequencies of the axial isomer of $(\text{CO})_4\text{FeFP}[\text{O}(\text{CCF}_3)_2\text{CN}]_2$ with those of $(\text{CO})_4\text{FeFP}(\text{OCH}_3)_2$ shows a shift to lower wavenumbers of about $20\text{--}35\text{ cm}^{-1}$ in the latter complex, suggesting that $\text{FP}(\text{OCH}_3)_2$ is a weaker π acid than $\text{FP}[\text{OC}(\text{CF}_3)_2\text{CN}]_2$. This could arise from the greater inductive effect of a $\text{OC}(\text{CF}_3)_2\text{CN}$ group over that of a OCH_3

group. An even more striking comparison is that of the $\nu_{\text{C=O}}$ stretching frequencies of complex 3 with those of the equatorial isomer of $(\text{CO})_4\text{FePF}_3$. The highest A_1 mode in the latter compound at 2101 cm^{-1} has been shifted to 2127 cm^{-1} in complex 3. The other bands have also been shifted to higher wavenumbers. This suggests that the ligand $\text{P}[\text{OC}(\text{CF}_3)_2\text{CN}]_3$ is a very strong π acid. The $\nu_{\text{C=O}}$ frequencies observed for complex 3 are higher than those observed for the complex cation $(\text{CO})_4\text{FeP}[\text{N}(\text{CH}_3)_2]_2^+$, which contains the cationic ligand $^+\text{P}[\text{N}(\text{CH}_3)_2]_2$. This indicates an increased π acidity of the fully substituted PF_3 ligand when compared to that of PF_3 itself.

An apparent similar effect was noted for several nickel carbonyl fluorophosphine complexes in which the fluorine in PF_3 was replaced by CF_3 groups.¹⁵ Thus for $(\text{PF}_3)_3\text{NiCO}$ the $\nu_{\text{C=O}}$ occurred at 2085 cm^{-1} while for $(\text{CF}_3\text{PF}_2)_3\text{NiCO}$ it occurred at 2092 cm^{-1} . The suggested explanation was that the amount of $\text{F}\rightarrow\text{P}$ π bonding was decreased by substitution, making phosphorus a better π acceptor while it was also becoming a better σ donor. This decrease was not observed upon disubstitution on phosphorus. Another example in which CF_3 groups were substituted for fluorine in PF_3 showed only a significant shift in the E mode between the compounds $\text{Mo}(\text{CO})_5\text{PF}_3$ and $\text{Mo}(\text{CO})_5\text{P}(\text{CF}_3)_3$ ¹⁶ (e.g.: $\text{Mo}(\text{CO})_5\text{PF}_3$, $A_1 = 2103\text{ cm}^{-1}$, $A'_1 = 2011\text{ cm}^{-1}$, and $E = 1989\text{ cm}^{-1}$; $\text{Mo}(\text{CO})_5\text{P}(\text{CF}_3)_3$, $A_1 = 2104\text{ cm}^{-1}$, $A'_1 = 2009\text{ cm}^{-1}$, and $E = 1996\text{ cm}^{-1}$). Although the changes observed in the carbonyl stretching frequencies in the above two examples are smaller in comparison with those observed for compound 3, it should be pointed out that the replacement of F by a CF_3 group is not completely analogous to the replacement of F by a $\text{OC}(\text{CF}_3)_2\text{CN}$ group, since the possibility of $\text{O}\rightarrow\text{P}$ π bonding exists in the latter case. Thus replacement of fluorine by the $\text{OC}(\text{CF}_3)_2\text{CN}$ group on phosphorus would be expected to decrease the π acidity of the phosphorus faster than replacement of fluorine by CF_3 groups if one assumes similar inductive effects (if the $\text{OC}(\text{CF}_3)_2\text{CN}$ group is less electronegative than the CF_3 group, an even faster lowering of the π acidity would be expected). This does not appear to be the case since the π acidity of the phosphorus in compounds 1, 2, and 3 apparently increases as substitution increases. The reason for this is not understood, and further studies are under way to shed some light on this problem.

Registry No. 1 (axial), 85185-65-5; 1 (equatorial), 85248-75-5; 2 (axial), 85185-66-6; 2 (equatorial), 85248-76-6; 3, 85185-67-7; 4 (axial), 85185-68-8; 4 (equatorial), 85248-77-7; $\text{FP}[\text{OC}(\text{CF}_3)_2\text{CN}]_2$, 85185-63-3; $\text{P}[\text{OC}(\text{CF}_3)_2\text{CN}]_3$, 85185-64-4; $\text{Fe}(\text{CO})_4\text{F}_2\text{PBr}$, 42886-00-0; $\text{Fe}(\text{CO})_4\text{F}_2\text{PCl}$, 60182-92-5; $\text{Fe}_2(\text{CO})_9$, 15321-51-4; $\text{NaOC}(\text{CF}_3)_2\text{CN}$, 6737-59-3; $\text{F}_2\text{POC}(\text{CF}_3)_2\text{CN}$, 20765-90-6; FPCl_2 , 15597-63-4; PCl_3 , 7719-12-2.

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Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

Synthesis and Reactivity of Dicationic Diolefin Complexes of the Type $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^2\text{-olefin})]_2[\text{BF}_4]_2$

Wesley W. McConnell, Gregory O. Nelson,*
and Michael E. Wright

Received August 9, 1982

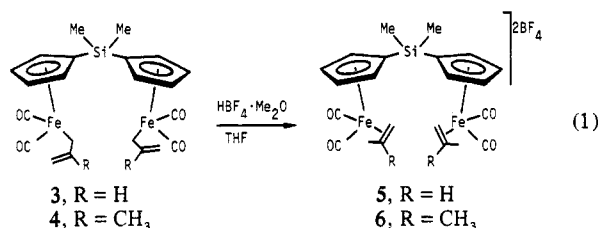
There is considerable attention being focused presently on the synthesis and study of dinuclear transition-metal com-

(14) This splitting was found to be 10 cm^{-1} in $[(\text{CH}_3)_2\text{N}]_2\text{PF}_2\text{Fe}(\text{CO})_4$ and $[(\text{C}_2\text{H}_5)_2\text{N}]_2\text{PF}_2\text{Fe}(\text{CO})_4$, 8 cm^{-1} in $(\text{PhPF}_2)\text{Fe}(\text{CO})_4$, and 12 cm^{-1} in $\text{C}_3\text{H}_9\text{NPf}_2\text{Fe}(\text{CO})_4$.

plexes.² A reasonable portion of this interest is concerned with how organic moieties interact with two metal centers in close proximity. Recent work in our laboratory has dealt with the chemistry of the dimethylsilyl (Me_2Si) bridged species $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{R}]_2$ ³ and $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})(\text{L})\text{I}]_2$ ($\text{L} = \text{PPh}_3$ and P(OPh)_3),⁴ which are dinuclear analogues of the well-studied systems $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ and $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{L})\text{I}$, respectively. In the dinuclear complexes, the Me_2Si unit behaves as a chemically noninteractive link between the two cyclopentadienyl rings and hence retains the metal centers in close proximity. We have noted in earlier studies that this latter effect can indeed cause subtle changes in their reactivity patterns when compared to those of their mononuclear analogues.^{3,4} The purpose of this note is to report the synthesis, characterization, and reactivity of the dicationic, diolefin complexes $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\eta^2\text{-olefin}]_2[\text{BF}_4]_2$, where olefin = propene and isobutylene.

Results and Discussion

Reaction of the dianion $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ (**2**) with the appropriate allylic chloride produces moderate isolated yields (ca. 30%) of the bis(η^1 -allyl) complexes **3** and **4**. These compounds are isolated as very air-sensitive red-yellow oils by low-temperature (-10°C) column chromatography (alumina III). Both **3** and **4** display characteristic ^1H NMR and IR spectral data in comparison to previously reported (η^1 -allyl)iron complexes.⁵



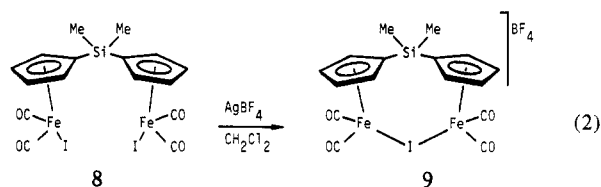
Complexes **3** and **4** are readily protonated by $\text{HBF}_4\cdot\text{Me}_2\text{O}$ in THF to give the expected cationic bis(η^2 -olefin) complexes **5** and **6**, respectively (eq 1).⁵ Due to the instability of **3** and **4**, we find it most convenient to avoid isolation of these intermediates and use them directly off the chromatography column. By this method we can obtain **5** and **6** in ca. 50% isolated yields on the basis of dianion **2**. These cationic bis-(η^2 -olefin) species **5** and **6** display characteristic ^1H and ^{13}C NMR spectra compared to those of their mononuclear counterparts. However, their reactivity patterns are not so clear-cut.

Rosenblum reported a ligand-exchange reaction worthy of comparison here. The isobutylene unit of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^2\text{-isobutylene})][\text{BF}_4]$ can readily exchange with less sterically hindered olefins upon heating.⁵ Similar treatment of **6** with several olefins does not induce exchange of the isobutylene moiety. For example, **6** is allowed to react with propene, cyclopentene, and *cis*-2-butene in 1,2-dichloroethane at 60°C or less for various time lengths ranging from 20 min to 24 h. In all cases only the diisobutylene complex **6** is recovered. Higher temperatures (65°C) results in degradation of the complex to an intractable red oil. A key point to note is that **6** is much less soluble in CH_2Cl_2 and $\text{ClCH}_2\text{CH}_2\text{Cl}$ than $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^2\text{-isobutylene})][\text{BF}_4]$. Even highly coordinating solvents such as CH_3NO_2 and CH_3CN , in which **6** is more soluble, give only starting material back when heated

to 60°C in the presence of olefins. From these results it is apparent that the η^2 -isobutylene moieties are not dissociating at temperatures of 60°C or less and that above 60°C an alternate reaction pathway leading to decomposition is predominant over the exchange reaction. It is not possible to say why **6** appears to be so inert to dissociation, but it is clear that the exchange route used in the mononuclear example will not be useful in the case of the dinuclear system **6**.

Reduction of **6** by NaBH_3CN produces the expected compound $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}(\text{CH}_3)_2)]_2$ (**7**) in 85% yield. However, treatment of **5** with NaBH_3CN in THF at 0°C gives a mixture of the η^1 -*n*-propyl and η^1 -isopropyl compounds in a ca. 1:1 ratio. The formation of the *n*-propyl group is surprising, since in the reduction of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^2\text{-propene})][\text{BF}_4]$ with NaBH_3CN only the η^1 -isopropyl product is observed.⁶

The lack of ability to exchange the isobutylene units of **6** led us to attempt another versatile method for olefin complexation, the halogen abstraction route.⁷ When $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{L})\text{X}$ ($\text{L} = \text{CO}$, PPh_3 , P(OPh)_3 ; $\text{X} = \text{Br}$, I), in the presence of excess olefin, is treated with AgBF_4 , olefin complexes of the type $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{L})(\eta^2\text{-olefin})][\text{BF}_4]$ are obtained. It is well-known that this takes place by formation of the very reactive intermediate $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})(\text{L})][\text{BF}_4]$ followed by rapid complexation of the two-electron olefin donor.⁸ However, in the absence of olefin, a cationic bridging halide complex is formed. An X-ray structure of one such compound, $[(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2)\text{I}][\text{BF}_4]$, has been completed.⁹ Furthermore, Foxman noted even in the presence of two-electron donors, namely ketones, that the formation of $[(\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2)_2\text{Br}][\text{PF}_6]$ is competitive when a high concentration of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$ is employed.¹⁰ This indicates that $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$ competes with the ketone for the two-electron donor site in the $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2][\text{PF}_6]$ species. It is therefore not too surprising that the only complex isolated, even in the presence of excess olefin, when $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{I}]_2$ (**8**) is treated with AgBF_4 , is the bridging iodonium salt $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2)_2\text{I}][\text{BF}_4]$ (**9**) (eq 2). As mentioned above, the silyl bridge in the diiodide **8** keeps the two iron coordination spheres in close proximity to one another. When one iodide is removed, the other iodide is in excellent position to bridge the two metal centers. Thus, complex **8** in CH_2Cl_2 is behaving like a highly concentrated solution of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$: a factor that prevents complexation of olefin.



In summary, this work shows that the bridged cationic bis(η^2 -olefin) complexes are available through the η^1 -allyl isomerization route and undergo normal reactions with reducing agents. Additionally, linking the two metal centers close to one another causes a divergence of reactivity from the mononuclear analogues in that the η^2 -isobutylene units of **6** do not exchange with less hindered olefins. Furthermore, the diiodide complex **8** acts as a highly concentrated solution of

- (1) To whom correspondence should be addressed at Tennessee Eastman Co., Kingsport, TN 37662.
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$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ and subsequently produces only the bridging iodonium system upon reaction with AgBF_4 in the presence of olefins.

Experimental Section

General Procedures. All reactions and subsequent manipulations were carried out by using standard Schlenk techniques under argon or purified nitrogen atmospheres. Solvents were routinely dried by standard procedures and stored under an inert atmosphere.¹¹ The NMR solvents were predried over 3-Å molecular sieves, subjected to three consecutive freeze-pump-thaw cycles, and then stored in a Schlenk flask under an inert atmosphere. In addition, NMR samples were routinely passed through a short column of Celite to remove finely divided decomposition particles.

Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian EM360, Bruker 250FT (at 250 MHz); ^{13}C NMR, Bruker 250FT (at 62.9 MHz); IR, Perkin-Elmer 281B or PE 398. NMR chemical shifts were reported in δ vs. Me_4Si with the CDCl_3 resonance in ^{13}C spectra assigned as 77.00 ppm. The reported ^{13}C NMR spectra were run with ^1H decoupling, and resonances may be assumed to be singlets unless multiplicity was specified (off-resonance spectra were run to confirm assignments). The compound $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2$ (**1**)³ and its dianion $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2]_2^{2-}$ (**2**)¹² were prepared by literature methods. The 3-chloropropene and 2-methyl-3-chloropropene were purchased from Aldrich and distilled prior to use. The $\text{HBF}_4\cdot\text{Me}_2\text{O}$ and NaBH_3CN were purchased from Aldrich and used without further purification.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)]_2$ (3**).** To 50 mL of THF containing 0.50 g (1.2 mmol) of **2** was added 1.0 mL (12 mmol) of $\text{ClCH}_2\text{CH}=\text{CH}_2$ at 0 °C with stirring. The reaction mixture was stirred for an additional 2 h at 0 °C, the solution filtered, and the solvent removed in vacuo at ambient temperature. The resulting oil was column chromatographed at low temperature (alumina III, -10 °C, pentane). The initial yellow band was collected and the solvent removed in vacuo to give a red-yellow oil identified by ^1H NMR and IR as **3**. ^1H NMR (CDCl_3): δ 6.32–5.5 (2, m, $\text{CH}=\text{CH}_2$), 5.00–4.28 (4, m, $\text{CH}_2=\text{CH}_2$), 4.72 (8, s, C_5H_4), 2.07 (4, d, $J = 9$ Hz, CH_3), 0.52 (6, s, SiCH_3). IR spectrum (cm^{-1} in CDCl_3): $\nu(\text{CO})$ 2002 and 1950.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{C}(\text{CH}_3)=\text{CH}_2)]_2$ (4**).** Compound **4** was synthesized by a method completely analogous to the preparation of **3** using 3-chloro-2-methylpropene as the allylic halide. Compound **4** was isolated after low-temperature chromatography as a red-yellow oil (0.23 g, 36%). ^1H NMR (CDCl_3): δ 4.73 (4, m, $\text{CH}=\text{CH}_2$), 4.51 (8, d, C_5H_4), 2.13 (4, s, CH_2), 1.78 (6, s, CH_3), 0.53 (6, s, SiCH_3). IR spectrum (cm^{-1} in CDCl_3): $\nu(\text{CO})$ 2002 and 1950.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CHCH}_3)]_2[\text{BF}_4]_2$ (5**).** A pentane solution containing **3** (obtained directly from the alumina column described above) was added dropwise to a solution of $\text{HBF}_4\cdot\text{Me}_2\text{O}$ (0.30 g, 2.4 mmol) at -10 °C with stirring. The resulting bright yellow precipitate was collected by filtration, washed with cold THF (10 mL \times 2), and dried under vacuum to yield pure **5** (0.36 g, 45%). ^1H NMR (acetone- d_6): δ 6.04, 5.83 (8, s, C_5H_4), 5.30 (2, m, $\text{CH}=\text{CH}_2$), 4.01 (2, d, $J = 8$ Hz, $\text{CH}_2=\text{CH}_2$), 3.63 (2, d, $J = 14$ Hz, $\text{CH}_2=\text{CH}_2$), 1.86 (6, d, $J = 6$ Hz, CH_3), 0.94 (6, s, SiCH_3). IR spectrum (cm^{-1} in CH_3NO_2): $\nu(\text{CO})$ 2072, 2030. ^{13}C NMR (CD_3NO_2): δ 211.23, 209.69 (CO), 96.39, 94.91 (C_5H_4), 89.17 ($\text{CH}=\text{CH}_2$), 56.91 ($\text{CH}_2=\text{CH}_2$), 22.37 (CH_3), -2.36 (SiCH_3).

Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{B}_2\text{F}_8\text{Fe}_2\text{O}_4\text{Si}$: C, 39.57; H, 3.92. Found: C, 39.65; H, 4.01.

Preparation of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CH}_2)]_2[\text{BF}_4]_2$ (6**).** Similar treatment of **4** with $\text{HBF}_4\cdot\text{Me}_2\text{O}$ (0.30 g, 2.4 mmol) at -10 °C gave complex **6** as a yellow solid (0.45 g, 53%). ^1H NMR (acetone- d_6): δ 6.13 (8, s, C_5H_4), 4.03 (4, s, CH_2), 1.98 (12, s, $(\text{CH}_3)_2\text{C}=\text{CH}_2$), 0.96 (6, s, SiCH_3). IR spectrum (cm^{-1} in CH_3NO_2): $\nu(\text{CO})$ 2067 and 2030. ^{13}C NMR (CD_3NO_2): δ 206.06, 203.31 (CO), 91.52, 90.26 (C_5H_4), 80.49 ($(\text{CH}_3)_2\text{C}=\text{CH}_2$), 48.86 (CH_2), 23.92 (CH_3), -7.91 (SiCH_3).

Anal. Calcd for $\text{C}_{24}\text{H}_{30}\text{B}_2\text{F}_8\text{Fe}_2\text{O}_4\text{Si}$: C, 41.43; H, 4.34. Found: C, 41.58; H, 4.38.

Reduction of **5 with NaBH_3CN .** To a 15 mL THF slurry of **5** (0.25 g, 0.38 mmol) at 0 °C was added NaBH_3CN (0.048 g, 0.76 mmol) with stirring. The reaction mixture was stirred for an additional 1 h at 0 °C and then slowly allowed to warm to room temperature. This mixture was filtered and the solvent removed to yield a red-yellow oil. The oil was column chromatographed (alumina III, hexane) and the initial yellow band collected. The hexane was removed under vacuum to give an air-sensitive red-yellow oil identified as a mixture of η^1 -*n*-propyl and η^1 -isopropyl isomers (0.15 g, 79%). The mixture gave ^1H NMR (CDCl_3) signals at δ 4.68 (C_5H_4), 2.55 (m, $J = 6$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.23 (d, $J = 6$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.23 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.78 (m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.38 (6, s, SiCH_3). IR spectrum (cm^{-1} in CDCl_3): $\nu(\text{CO})$ 1990 and 1940.

Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{Fe}_2\text{O}_4\text{Si}$: C, 53.53; H, 5.79. Found: C, 53.25; H, 5.69.

Reduction of **6 to $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}(\text{CH}_3)_2)]_2$ (**8**).** Complex **8** (0.38 mmol) was prepared by a method analogous to the preparation of complex **7**. The product was isolated as a red-yellow oil (0.17 g, 85%) and identified as **8**. ^1H NMR (CDCl_3): δ 4.70 (8, s, C_5H_4), 1.25 (6, m, $\text{CH}_2\text{CH}(\text{CH}_3)_2$), 0.80 (12, d, $J = 5$ Hz, CH_3), 0.3 (6, s, SiCH_3). IR spectrum (cm^{-1} in CDCl_3): $\nu(\text{CO})$ 1990 and 1942. ^{13}C NMR (CDCl_3): δ 217.88 (CO), 92.87, 89.33, 85.45 (C_5H_4), 34.81 (CH), 26.25 (CH_3), 13.68 (CH_2), -1.44 (SiCH_3).

Anal. Calcd for $\text{C}_{24}\text{H}_{32}\text{Fe}_2\text{O}_4\text{Si}$: C, 55.14; H, 6.39. Found: C, 54.98; H, 6.15.

Preparation of $[\text{Me}_2\text{Si}(\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2)_2][\text{BF}_4]$ (9**).** A solution of $\text{Me}_2\text{Si}[\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{I}]_2$ (**8**) (0.50 g, 0.80 mmol) in 25 mL of CH_2Cl_2 was treated with AgBF_4 (0.35 g, 1.9 mmol) at 30 °C. After 5 min of reaction the color had changed from brown to deep red with contamination of the solution by AgI precipitation. The mixture was filtered, the solvent was removed under vacuum, and the residue was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give pure **9**. The results of this reaction were the same when a large excess of olefin was present when the AgBF_4 was added. ^1H NMR (acetone- d_6): δ 6.10, 5.47 (8 m, C_5H_4), 0.80 (6, s, SiCH_3). IR spectrum (cm^{-1} in CH_2Cl_2): $\nu(\text{CO})$ 2037 and 1995. ^{13}C NMR (acetone- d_6): δ 211.94 (CO), 97.08, 91.33, 84.24 (C_5H_4), -2.20 (SiCH_3).

Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{BF}_4\text{Fe}_2\text{IO}_4\text{Si}$: C, 30.81; H, 2.26; I, 20.34. Found: C, 30.85; H, 2.27; I, 20.18.

Acknowledgment is made to the NSF (Grant CHE-8102918) for support of this work.

Registry No. **2**, 85319-98-8; **3**, 85319-99-9; **4**, 85320-00-9; **5**, 85320-02-1; **6**, 85320-04-3; **7**, 85320-09-8; **8**, 80399-47-9; **9**, 85320-07-6; $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^1\text{-CH}_2\text{CH}_2\text{CH}_3)]_2\text{SiMe}_2$, 85320-08-7; $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\eta^1\text{-CH}(\text{CH}_3)_2)]_2\text{SiMe}_2$, 85320-05-4; $\text{ClCH}_2\text{CH}=\text{CH}_2$, 107-05-1; 3-chloro-2-methylpropene, 563-47-3.

Contribution No. 6741 from the Department of Chemistry, California Institute of Technology, Pasadena, California 91125

Crystal Structure of a Molybdenum(VI) Compound with a Tetradentate N_2S_2 Ligand: Re-refinement in a Higher Symmetry Space Group

Richard E. Marsh* and Anna Toy

Received October 13, 1982

The crystal structure of [bis(*p*-methoxyphenyl)diazenedio] [*N,N'*-dimethyl-*N,N'*-bis(mercaptoethyl)ethylenediamine]molybdenum(VI) has been described in space group *Cc* (monoclinic; *a* = 22.557 (2), *b* = 8.483 (3), *c* = 18.030 (2) Å; β = 133.25 (1)°) and was refined to an *R* of 0.043 for 1505 reflections with $I(\text{obsd}) \geq 3.0\sigma(I(\text{obsd}))$.¹ Surprising

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