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Preliminary communication

FLUXIONAL BEHAVIOR OF $(CO)_4Fe(\mu\text{-}AsMe_2)Mo(CO)_2(C_5H_5)$

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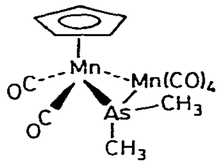
Summary

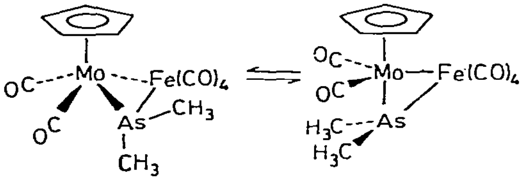
The ^1H and ^{13}C NMR spectra of the heterobimetallic compound $(CO)_4Fe(\mu\text{-}AsMe_2)Mo(CO)_2(C_5H_5)$ reveal three different fluxional processes.

In connection with studies of the possible use of heterobimetallic complexes as CO and alkene hydrogenation catalysts [1], we have examined the temperature dependent ^1H and ^{13}C NMR spectra of $(CO)_4\overline{Fe(\mu\text{-}AsMe_2)}Mo(CO)_2(C_5H_5)$ (1) [2]. Three independent fluxional processes have been identified.

Temperature dependent NMR spectra. The 270 MHz ^1H NMR spectra of 1 at −71°C in THF-d_8 consists of a singlet at δ 5.41 ppm for the C_5H_5 group and two singlets at δ 1.94 and 2.09 ppm for the non-equivalent methyl groups on arsenic. This spectrum is consistent with the structure shown for 1 in which one methyl is *syn* to the C_5H_5 group and one is *anti*. The structure of 1 is probably very similar to that of $(CO)_4\overline{Mn(\mu\text{-}AsMe_2)}Mn(CO)_2(C_5H_5)$ determined by X-ray crystallography [3].

As the temperature is increased, the C_5H_5 resonance remains sharp but the methyl resonances broaden, coalesce at about −43°C, and then become a sharp singlet at δ 1.99 above 15°C*. Comparison of observed and calculated spectra





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*For the $AsMe_2$ fragment, ^1H data (temperature, multiplicity, line width at half height, rate constant, $\Delta G^{\ddagger}$) follow: −53°C, 2 singlets, 7.5 Hz, 15 sec^{-1}, 11.6 kcal mol^{-1}; −48°C, 2 singlets, 15 Hz, 33 sec^{-1}, 11.5 kcal mol^{-1}; −43°C, singlet, 30 Hz, 110 sec^{-1}, 11.2 kcal mol^{-1}; −37.5°C, singlet, 21 Hz, 140 sec^{-1}, 11.3 kcal mol^{-1}; −33°C, singlet, 13 Hz, 220 sec^{-1}, 11.4 kcal mol^{-1}; −23°C, singlet, 9 Hz, 350 sec^{-1}, 11.6 kcal mol^{-1}; 15°C, singlet, 2 Hz.

[4] indicate that the process which exchanges the methyl group has $\Delta G^{\ddagger}$ = 11.4 ± 0.2 kcal mole^{-1}.

The exchange of the arsenic methyl groups of 1 can also be observed by ^{13}C NMR. The proton decoupled 50.1 MHz ^{13}C spectrum of 1 at −74°C in acetone-d_6 containing 0.07 M Cr(acac)$_3$ consists of two singlets at δ 14.5 and 17.8 ppm assigned to the arsenic methyl groups, a singlet at δ 91.0 ppm assigned to the C_5H_5 unit, a singlet at δ 211.7 ppm for all four of the carbonyl groups on iron, and two singlets at δ 241.1 and 242.4 ppm for the non-equivalent carbonyl groups on molybdenum. Upon warming from −74°C, the resonances for the arsenic methyl groups broaden, coalesce at about −25°C, and become a sharp singlet at −3°C*. Comparison of observed and calculated ^{13}C spectra indicates that the process which exchanges the arsenic methyl groups has $\Delta G^{\ddagger}$ = 11.2 ± 0.3 kcal mole^{-1} in close agreement with the value obtained from ^{1}H NMR.

The molybdenum carbonyl resonances in the ^{13}C NMR also exhibit temperature dependence. Upon warming from −74°C, the molybdenum carbonyl resonances broaden, coalesce at about −30°C, and becomes a broad singlet (δ 241.4 ppm) at −21°C**. Comparison of observed and calculated ^{13}C spectra indicates that the process that interconverts the molybdenum carbonyls has $\Delta G^{\ddagger}$ = 11.4 ± 0.2 kcal mol^{-1}. Since the measured free energies of activation for exchange of the arsenic methyl groups and for exchange of the molybdenum carbonyl groups are not significantly different, the same molecular rearrangement is probably responsible for both exchange processes.

Although the four carbonyls on iron in 1 are all in chemically different environments, even at −74°C the ^{13}C resonances for all four carbonyls is a singlet (line width 13 Hz) no broader than the other peaks in the ^{13}C spectrum. While it is possible that the four carbonyl groups all accidentally have the same chemical shift, it seems more likely that the environments of the Fe(CO)$_4$ carbonyl groups are exchanged in a very low activation energy process***.

The high temperature ^{13}C NMR spectra of 1 in acetone-d_6 reveal a third process in which carbonyl groups are exchanged between iron and molybdenum. The process is first noticeable at −3°C where the line width of the Mo(CO)$_2$ (28 Hz) and Fe(CO)$_4$ (15 Hz) are significantly broader than the C_5H_5 group (6 Hz). As expected for a process which exchanges 2 CO's on Mo with 4 CO's on Fe, the resonance due to Mo(CO)$_2$ broadens at a lower temperature than the resonance for Fe(CO)$_4$. At 20°C, the line width for Mo(CO)$_2$ is very

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*For the AsMe$_2$ fragment, ^{13}C NMR data (temperature, multiplicity, line width, rate constant, $\Delta G^{\ddagger}$) follow: −45°C, 2 singlets, 44 Hz, 100 sec^{-1}, 11.2 kcal/mol: −21°C, singlet, 50 Hz, 1000 sec^{-1}, 11.2 kcal/mol: −3°C singlet, 11 Hz; 20°C, singlet, 5.5 Hz.

**For the Mo(CO)$_2$ fragment, ^{13}C NMR data (temperature, multiplicity, line width, rate constant, $\Delta G^{\ddagger}$) follow: −45°C, 2 singlets, 32 Hz, 59 sec^{-1}, 11.4 kcal/mol; −21°C, singlet, 16 Hz, 580 sec^{-1}, 11.5 kcal/mol.

***If the singlet observed at −74°C for the iron carbonyls was due to rapid exchange between two peaks which differed in chemical shift by 1.0 ppm, then $\Delta G^{\ddagger}$ for the exchange process must be less than 8.8 kcal mol^{-1}.

large and the line width for $Fe(CO)_4$ is 53 Hz. Above 45°C, the $Mo(CO)_2$ resonance is too broad to be detected and above 74°C the $Fe(CO)_4$ resonance is also too broad to be seen*. Comparison of observed and calculated spectra indicate $\Delta G^{\ddagger} = 14.2 \pm 0.6$ for this high temperature exchange of carbonyls between iron and molybdenum**.

Reaction of 1 with $P(CH_3)_3$. In order to determine if a coordinatively unsaturated metal species might be responsible for one of these three independent exchange processes, the rate of reaction of 1 with $P(CH_3)_3$ was studied. The reaction of 1 with $P(CH_3)_3$ in benzene-d_6 at 20°C was followed by ^1H NMR and found to give $(CO)_4Fe(\mu\text{-}AsMe_2)Mo(CO)_2(PMe_3)(C_5H_5)$ (2), which has been previously characterized by Vahrenkamp [5]. The rate of formation of 2 in tetrahydrofuran at 25.0°C was followed by visible spectroscopy at 510 nm and was found to depend on the concentrations of both 1 and $P(CH_3)_3$; the second order rate constant at 25.0°C is $1.40 \pm 0.05 \times 10^{-4}\ M^{-1}\ sec^{-1}$***. Thus the rate of reaction of 1 with $P(CH_3)$ is much slower than the process that exchanges the environments of arsenic methyl groups and of the molybdenum carbonyl groups on 1. Moreover, the observation of second order kinetics does not require that 1 be undergoing spontaneous cleavage of its metal—metal bond at room temperature followed by phosphine trapping. Rather, this observation is more consistent with direct attack of $P(CH_3)_3$ on 1.

Nature of fluxional processes. The four chemically different carbonyl groups on iron are equivalent in the ^{13}C NMR at −74°C. While the NMR equivalence might be the result of accidental degeneracy of the chemical shifts, it is likely that the iron carbonyls exchange environment by a very low activation energy process. Other substituted tetracarbonyliron compounds also show a single ^{13}C NMR resonance [7]. A solution of $Fe(CO)_5$ has a single ^{13}C NMR resonance at −170°C [8], and spectra of solid $Fe(CO)_5$ suggest that exchange of axial and equatorial carbonyls even occurs in the solid [9]. Finke has found that a rapid fluxional process averages the environment of the carbonyl groups in the heterobimetallic complex $(C_5Me_5)Rh(\mu\text{-}PMe_2)_2Mo(CO)_4$ [10].

The coordination geometry about the molybdenum atom of 1 can be thought of as a square pyramid with the C_5H_5 unit at the apex. The nonequivalent environments of the arsenic methyls and molybdenum carbonyls can be exchanged by isomerization of 1 to its enantiomer via 3, a symmetrical trigonal bipyramidal intermediate (or transition state) which has a plane of

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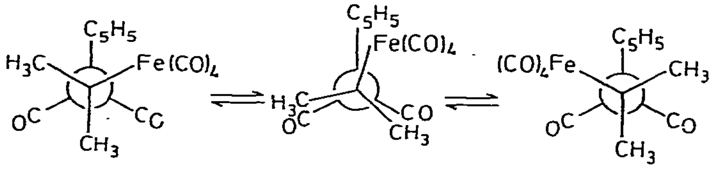
* Line simulation calculations reveal that at −3°C, the rate constant is 25 sec^{-1}, and $\Delta G^{\ddagger}$ 14.0 kcal mol^{-1}. At 20°C, the calculated rate constant is 140 sec^{-1} ($\Delta G^{\ddagger}$ 14.3 kcal mol^{-1}). At 45°C, the line width of the $Fe(CO)_4$ resonance is about 120 Hz. The observation that the resonances for $Mo(CO)_2$ at 45°C (and for $Mo(CO)_2$ and $Fe(CO)_4$ at 74°C) were too broad to be observed is in agreement with our calculations of the expected spectra for exchange between sites which have large chemical shift differences (~1480 Hz).

** The exchange has a higher activation energy in less polar solvents. At 62°C in benzene-d_6, the line widths are 42 Hz and 154 Hz for $Fe(CO)_4$ and $Mo(CO)_2$, respectively. This corresponds to a rate of 108 sec^{-1}; $\Delta G^{\ddagger}$ 16.6 ± 0.6 kcal mol^{-1}.

***Poë et al. [6] have recently reported detailed kinetic studies of ligand addition to $(CO)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$ and have also found second order kinetics. A strong dependence of k_2 on the nature of the incoming ligand was interpreted as evidence for rate-determining nucleophilic attack.



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symmetry passing through Mo, Fe, and As*. Newman projections looking down the As—Mo bond are also useful is visualizing the process that exchanges methyl groups and molybdenum carbonyl groups. Faller [11] has observed *cis-trans* interconversion of $(C_5H_5)Mo(CO)_2LR$ compounds, and has explained the isomerization in terms of a square pyramid-trigonal bipyramid-square pyramid interconversion.

The high temperature process which exchanges carbonyl groups between iron and molybdenum could occur via several different intermediates (or transition states). One possibility is the reversible formation of the triply bridging species $(CO)_3Fe(\mu\text{-}AsMe_2)(\mu\text{-}CO)_2Mo(CO)(C_5H_5)$ which accomplishes the exchange in a simple manner. This process is similar to the one suggested for $[C_5H_5Fe(CO)_2]_2$ [12]. Alternatively, simultaneous cleavage of the arsenic bridge and formation of a carbonyl bridge could lead to either $(CO)_3(AsMe_2)\text{-}Fe(\mu\text{-}CO)Mo(CO)_2(C_5H_5)$ or $(CO)_4Fe(\mu\text{-}CO)Mo(AsMe_2)(CO)(C_5H_5)$; then exchange between bridging and terminal CO's could accomplish the required exchange process.

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*Of course, there is no way to distinguish between trigonal bipyramids having As or Fe as the axial group.