ORGANOMETALLICS

Site selectivity in the reaction of (.eta.2-1,3-cyclohexadiene)Fe(CO)3-.bul. with hydrogen and deuterium atoms

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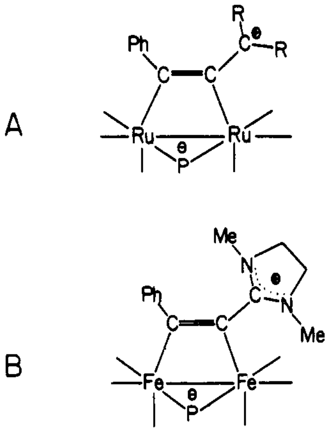

Figure 7. Possible zwitterionic transition state involved in the exchange mechanism (A) and the structure of Fe$_2$(CO)$_6$[μ_2-η^2-C(CNMe(CH$_2$)$_2$NMe)CPh](μ-PPh$_2$) (B).

able to show that the rate of isomerization was dependent on pyridine concentration, addition of excess pyridine to toluene-d_8 solutions of **3a** had no effect on the line shape of the ^{1}H NMR spectrum at 30 °C, indicating no rate increase. This is interpreted as indicating that the generation of a similar μ-alkylidene intermediate is not responsible for the fluxional behavior of **3a**.

A third possibility (mechanism III) involves an interchange of R groups on the allenyl group by rotation about the exoskeletal bond C(8)–C(9). This exchange process, which is consistent with the ^{1}H and ^{31}P data and not inconsistent with the ^{13}C spectra, can be envisaged as occurring via a zwitterionic transition state in which C(8)–C(9) is a single bond, C(9) is carbocationic, and the negative end of the dipole, formally on C(7) (or C(8)), is delocalized into the Ru$_2$P(CO)$_6$ skeleton (Figure 6).

Evidence in support of mechanism III is that the activation energy for R = CH$_3$ is lower than for R = H. Using the relationships $k = \pi\Delta\nu/(2)^{1/2}$ and $k = (k_bT/h)\exp(-\Delta G^{*}/RT)$ values of ΔG^{*} = 18.7 and 15.6 kcal mol^{-1} for **3a** and **3b**, respectively are obtained. The latter values are calculated for coalescence temperatures of 30 ± 1 °C for **3b** and a value of 100 ± 3 °C for **3a**. This order is entirely consistent with the ability of methyl groups to enhance the stabilization of carbocations relative to hydrogen substituents.

The most compelling evidence for mechanism III is found in the isolation and characterization of Fe$_2$(CO)$_6$[μ_2-η^2-C(CNMe(CH$_2$)$_2$NMe)CPh](μ-PPh$_2$) depicted in Figure 7B. The X-ray structure of this compound can essentially be considered a snapshot of the proposed transition state. The primary structural features of the latter have already been described,[33] but important points relevant to this discussion need a brief mention here. The C(9)–N bonds are short with an average length of 1.319 (20) Å indicative of multiple-bond character. This is further illustrated by planar stereochemistry about each nitrogen atom. The C(8)–C(9) bond is clearly devoid of multiple-bond character as shown by a bond length of 1.550 (12) Å, while the C(7)–C(8) interaction results in a bond length of 1.21 (3) Å, justifying the presence of strong multiple bonding. The Fe(1)–C(7) and Fe(2)–C(8) bond lengths are essentially identical with values of 2.09 (3) and 2.08 (2) Å, respectively. The angles about the nitrogens N(1) and N(2) are 358.99 and 359.99° clearly showing their planar environment. Taken as a whole, these results point to a delocalized positive charge distributed over the two nitrogen atoms with the negative charge delocalized in the iron core. Such a representation presumably allows free rotation about the C(8)–C(9) bond and thus nicely represents a model to explain the exchange of R groups in **3**.

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Registry No. 2, 78163-18-5; **3a**, 101834-73-5; **3b**, 101834-74-6; **3c**, 101834-75-7; N$_2$CH$_2$, 334-88-3; N$_2$C(CH$_3$)$_2$, 2684-60-8; N$_2$CPh$_2$, 883-40-9.

Supplementary Material Available: Tables S1A and S1B, anisotropic thermal parameters (×10^3) for molecules A and B of Ru$_2$(CO)$_6$[μ_2-η^2-Ph$_2$C=C=C(Ph)](μ-PPh$_2$) (**3c**), and Table S2, structure factors for molecules A and B of **3c** (32 pages). Ordering information is given on any current masthead page.

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Site Selectivity in the Reaction of (η^2-1,3-Cyclohexadiene)Fe(CO)$_3^{-\bullet}$ with Hydrogen and Deuterium Atoms

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Thermal energy electrons attach to (η^4-1,3-c-C$_6$H$_8$)Fe(CO)$_3$ generating (η^2-1,3-c-C$_6$H$_8$)Fe(CO)$_3^{-\bullet}$ (1). Reaction of 1 with H atoms gave the fragmentation product ions (OC)$_3$FeH$^-$, (OC)$_3$Fe$^{-\bullet}$, and (C$_6$H$_8$)Fe(CO)$_2$(H)$^-$ in the ratio of 75/20/5. When 1 was allowed to react with D atoms, the major fragment ion product was observed to be composed of (OC)$_3$FeD$^-$ (69%) and (OC)$_3$FeH$^-$ (31%). These results are interpreted in terms of principal formation of the Fe–H(D) bond as the primary process with some intramolecular rearrangement (H/D exchange) occurring prior to unimolecular fragmentation of the excited adduct negative ions.

The reactions of organometallic complexes with reactive atomic species (e.g. H, D, N, O) is an area limited to gas-phase investigations. Interest in such reactions extends from (a) their use to generate new, unique structures for further study to (b) their application in structure characterization of the original complex. The latter application would be especially useful in gas-phase studies of ionic complexes where mass and isotopic analysis is the principal spectroscopic tool used for identification of the complex. The present study makes use of the fact that the energy of the new bond (e.g., M–H) is deposited in the resultant excited adduct. If $D(L_xM\text{–}H)$ exceeds $D(L_{x-1}(H)M\text{–}L)$, fragmentation with loss of L will occur; where different ligands L and L′ are present, the loss of L vs. L′ is related to their dissociation energies in the excited adduct.

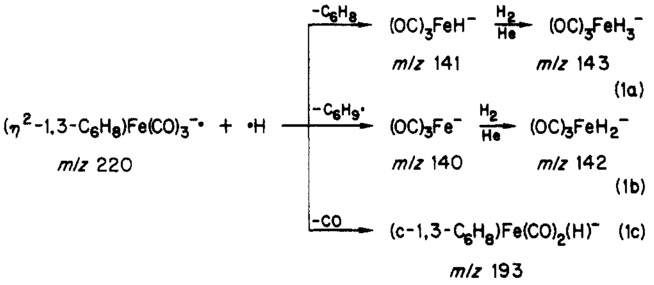
Our initial study in this area was directed at interest (a) and involved the reaction of the 17-electron $(OC)_4Fe^{-}\cdot$ with H atoms; equal amounts of $(OC)_3FeH^-$ and $(OC)_3Fe^{-}\cdot$ were the primary products.[1] We now report the results of the reactions of the 17-electron complex (η^2-1,3-cyclohexadiene)$Fe(CO)_3^{-}\cdot$ with hydrogen and deuterium atoms which demonstrate that the major primary bond-forming site in the complex is at iron. This is significant in light of the recent report of Lane and Squires,[2] who showed that hydride ion adds to the exo face of the benzene ring in $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ yielding $(OC)_3CrH^-$ as the anion fragmentation product.

Experimental Section

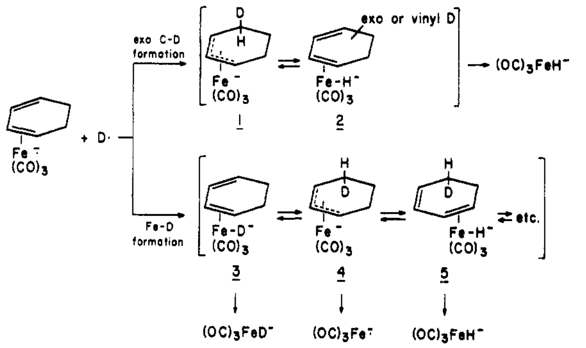
$(\eta^2\text{-1,3-c-}C_6H_8)Fe(CO)_3^{-}\cdot$ (*m/z* 220) was continuously generated by attachment of thermal electrons to $(\eta^4\text{-1,3-c-}C_6H_8)Fe(CO)_3$ in a fast flow of helium buffer gas (P_{He} = 0.5 torr, $\bar{v}$ = 80 m/s, 298 K) in the upstream end of our previously described flowing afterglow apparatus.[1,3] The η^2-diene structure of *m/z* 220 is assigned based on the characterization of this anion radical in the condensed phase[4] and its structural analogy to $(\eta^2\text{-1,3-}C_4H_6)Fe(CO)_3^{-}\cdot$ previously reported in the gas phase.[5] Following thermalization of the *m/z* 220 ions by numerous collisions with the buffer gas in the next 70 cm of the flow tube, the ions interact with a mixture of H atoms and H_2 added via a gas inlet in the final 65 cm of the flow tube. The H atoms are generated by passing H_2 through a glass tube inside of a microwave discharge cavity. The flow is maintained by a large, fast pumping system but is sampled into a differentially pumped compartment (~10^{-7} torr) containing a quadrupole mass filter and electron multiplier which continuously monitor the ion composition of the fast helium flow.

Results and Discussion

The three primary fragmentation products observed from the reaction of $(\eta^2\text{-c-1,3-}C_6H_8)Fe(CO)_3^{-}\cdot$ with H atoms are a major amount of $(OC)_3FeH^-$ (*m/z* 141) and lesser quantities of $(OC)_3Fe^{-}\cdot$ (*m/z* 140) and $(\eta^4\text{-c-1,3-}C_6H_8)Fe(CO)_2(H)^-$ (*m/z* 193) (eq 1). The coordinatively unsaturated fragment ions *m/z* 140 and 141 undergo secondary (termolecular) addition reactions with H_2 yielding the hydrides *m/z* 142 and 143, respectively,[1] while *m/z* 193 was stable to these conditions. The latter result suggests that ion *m/z* 193 has the 18-electron η^4-diene structure. At the smallest H atom/H_2 flow used where the H_2 adducts *m/z* 142 and 143 were only just observed, the ratio of *m/z* 140, 141, and 193 was 20/75/5, respectively. That the major fragmentation channels (1a) and (1b) involve loss of the cyclohexadiene ligand with only minor loss of CO (eq 1c) agree with the η^2-diene structure of the starting ion *m/z* 220[4,6] and in the intermediate excited adduct.



Scheme I



Of the three primary products from reaction 1, only the hydride *m/z* 141 carries with it information on where the H atom originally binds to the complex *m/z* 220 and any subsequent processes occurring in the excited adduct. This binding site can be probed by using D atoms instead of H atoms (see Scheme I). Bond formation of the D-atom to ion *m/z* 220 is possible by direct bonding to iron or addition to the diene or a carbonyl ligand. From the reported ESR spectrum of $(\eta^2\text{-1,3-}C_6H_8)Fe(CO)_3^{-}\cdot$, the small ^{13}C coupling (three equivalent CO ligands), and the large *g* factors and line widths compared to organic radicals strongly suggest that the unpaired electron is mainly on Fe in the complex.[4] Further, only the hydrogens of one of the double bonds of the diene exhibited resolvable hyperfine structure.

Therefore, approach of the D atom from the endo face of the 17-electron, iron-centered anion radical kinetically would strongly favor Fe–D bond formation.[9] The resulting fragmentation could vary from exclusive formation of $(OC)_3FeD^-$ from immediate decomposition of excited adduct 3 to a ratio of $[(OC)_3FeD^-)/(OC)_3FeH^-)]$ = 0.5 if the rearrangement occurs with complete equilibration of the D and the two endo Hs in 4 prior to unimolecular fragmentation of these adducts.[10] Addition of the D atom to the exo face of the diene yields the η^3-allyl complex 1 which can *only* rearrange an endo H to iron forming 2. Thus, only $(OC)_3FeH^-$ could be formed by this exo addition pathway.

As the signal for *m/z* 220 decayed with increasing flows of D atoms/D_2, no H/D exchange in the diene ligand of the starting ion was observed. At the lowest flow of D atoms/D_2 used in this study to minimize formation of the secondary products *m/z* 144–146 from addition of D_2 to

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[2] Lane, K. R.; Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 6403–6404.

[3] (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123–4128. (b) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *Ibid.* **1980**, *102*, 6491–6498.

[4] (a) Krusic and San Filippo (Krusic, P. J.; San Filippo, J. *J. Am. Chem. Soc.* **1982**, *104*, 2645–2647) characterized the parent anion radical formed by reduction of $(\eta^4\text{-1,3-c-}C_6H_8)Fe(CO)_3$ in THF as the 17-electron (η^2-diene) complex. (b) Private communication from Dr. Paul Krusic.

[5] McDonald, R. N.; Schell, P. L.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 5578–5579.

[6] $D^0[(OC)_4Fe\text{–}(C_2H_4)]$ = 24 kcal/mol[7] and $D^0[(OC)_4Fe\text{–}(CO)]$ = 41.5 ± 2 kcal/mol for the neutral complexes.[8]

[7] Conner, J. A. *Top. Curr. Chem.* **1977**, *71*, 17–110.

[8] Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905–3912.

[9] Whitesides and Arhart (Whitesides, T. H.; Arhart, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 5296–5298) reported the acid–base analogue of the present radical–radical coupling. These authors observed stereospecific H/D exchange of only the two endo hydrogens in the 1,3-cyclohexadiene ligand when $(\eta^4\text{-1,3-c-}C_6H_8)Fe(CO)_3$ was dissolved in CF_3CO_2D.

[10] The limiting $[(OC)_3FeD^-/(OC)_3FeH^-]$ = 0.5 is obtained if rearrangement of the deuterium in 3 can occur to the uncoordinated double bond forming 4. If the deuterium rearrangement is restricted between iron and the coordinated double bond in 3, $[(OC)_3FeD^-/(OC)_3FeH^-] \geq 1$ will be observed.

$(OC)_3Fe^{-}\cdot$, $(OC)_3FeD^{-}\cdot$, and $(OC)_3FeH^{-}\cdot$ and possible H/D exchange in $(OC)_3FeH^-$ (m/z 141),[1] the ratio $[(OC)_3FeD^-/(OC)_3FeH^-)] = 2.2$.

The large amount of $(OC)_3FeD^-$ formed in this reaction requires that the major bond-forming process is that of Fe–D formation yielding **3**.[10] However, the significant amount of $(OC)_3FeH^-$ produced could arise from rearrangement of **1** → **2** or **3** → **5** followed by fragmentation. Since the rearrangement of **1** → **2** is the microscopic reverse of the **3** → **4** rearrangement, it is reasonable that partial H/D exchange (via diene isomerization **3** → **4** → **5**) is competitive with unimolecular fragmentation of **3**. While we cannot exclude minor formation of **1** in this reaction, the presence of **1** is not required to account for the observed products.

The minor product m/z 193 formed in the reaction of $(\eta^2\text{-}1,3\text{-}C_6H_8)Fe(CO)_3^{-}\cdot$ (m/z 220) with H atoms (eq 1c) increases by 1 amu to m/z 194 in the reaction of m/z 220 with D atoms. The overall process is substitution of a CO ligand by the H or D atom. Three structures were considered possible for the negative ion m/z 193, the 18-electron species $(\eta^4\text{-}1,3\text{-}C_6H_8)Fe(CO)_2(H)^-$, and the two 16-electron complexes $(\eta^4\text{-}1,3\text{-}C_6H_8)Fe(CO)(CHO)^-$ and $(\eta^3\text{-}C_6H_9)Fe(CO)_2^-$. However, the latter two 16-electron complexes would be expected to readily add H_2 in a secondary reaction yielding the corresponding dihydrides as we have observed with other coordinatively unsaturated complex negative ions, e.g., $(OC)_4Mn^-$,[11] $(OC)_3Fe^{-}\cdot$,[12] and $(\eta^4\text{-}1,3\text{-}C_4H_6)Fe(CO)^{-}\cdot$.[5] The fact that m/z 193 (or 194) does not react with H_2 (or D_2) under these conditions or with extended reaction times (changing $\bar{v}$ from 80 to 32 m/s) eliminates the two 16-electron structures for m/z 193 from further consideration. Since some H/D rearrangement may have occurred in m/z 194, this anion may be composed of a mixture of $(\eta^4\text{-}1,3\text{-}C_6H_8)Fe(CO)_2(D)^-$ and $(\eta^4\text{-}1,3\text{-}C_6H_7D)Fe(CO)_2(H)^-$.

The fact that H/D exchange was not observed in unreacted m/z 220 suggests that the fragmentation/rearrangement of **3** occurs on every bond-forming collision. The source of the $(OC)_3Fe^{-}\cdot$ fragmentation product in these reactions appears to be the η^3-allyl ion **4** which decomposes by loss of the cyclohexenyl radical. Therefore, formation of the three primary negative ion products in the reaction of $(\eta^2\text{-}1,3\text{-}C_6H_8)Fe(CO)_3^{-}\cdot$ with H atoms are readily explained via initial production of a single, vibrationally excited intermediate $[(\eta^2\text{-}1,3\text{-}C_6H_8)Fe(CO)_3(H)^-]^*$. In the reaction of m/z 220 with D atoms, **3** is the intermediate and H/D exchange between Fe and the diene ligand and decarbonylation (→ m/z 194) are only modestly competitive with loss of the cyclohexadiene ligand from the excited intermediate.

We conclude that the reaction of $(\eta^2\text{-}1,3\text{-}C_6H_8)Fe(CO)_3^{-}\cdot$ with H and D atoms occurs principally (or exclusively) by initial formation of the Fe–H(D) bond. This is in contrast to the gas-phase reactions of various anions with neutral transition-metal carbonyl complexes which demonstrated that nucleophilic addition to the carbonyl[13] and other ligands (e.g., $\eta^6\text{-}C_6H_6$)[2] were the low-energy pathways. We expect to contribute further to the development of bond-forming induced decomposition (BFID) reactions between anions and reactive atomic species as a tool to aid in structural assignments of gas-phase negative ions.

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Registry No. $(\eta^4\text{-}1,3\text{-}c\text{-}C_6H_8)Fe(CO)_3$, 12152-72-6; $(\eta^2\text{-}1,3\text{-}c\text{-}C_6H_8)Fe(CO)_3^{-}\cdot$, 101471-50-5; H, 12385-13-6; D, 16873-17-9.

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[12] McDonald, R. N.; Chowdhury, A. K.; Schell, P. L. *J. Am. Chem. Soc.* **1984**, *106*, 6095–6096.

[13] Lane, K. R.; Sallans, L.; Squires, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5369–5375 and references therein.

A Convenient Synthesis of Symmetrical and Unsymmetrical 1,2-Bis(phosphino)benzenes as Ligands for Transition Metals

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The reaction of 1,2-bis(phosphino)benzene with 6 equiv of phosgene gives 1,2-bis(dichlorophosphino)benzene (**4**) in 45–55% yields. Species **4** reacts with 2 equiv of *t*-BuMgCl or PhZnCl to give 1,2-bis(*tert*-butylchlorophosphino)- (**5a**) and 1,2-bis(phenylchlorophosphino)benzene (**5c**), respectively. The former can be isolated in 56% yield as the $MgCl_2$ adduct, but **5c** must be reduced to 1,2-bis(phenylphosphino)benzene in order to facilitate isolation. The bis(secondary phosphine) 1,2-bis[(2,4,6-trimethylphenyl)phosphino]benzene (**6g**) was prepared in good yield from the reaction of **4** and the organozinc reagent obtained from (2,4,6-trimethylphenyl)magnesium bromide and zinc chloride, followed by LAH reduction. Compounds **5a,c** react readily with 2 equiv of MeMgBr to give the corresponding symmetrical 1,2-bis(tertiary phosphino)benzenes in high yields. Reaction of **4** with 1 equiv of PhZnCl or *t*-BuZnCl gives 1-(phenylchlorophosphino)- (**8a**) or 1-(*tert*-butylphosphino)-2-(dichlorophosphino)benzene (**8b**), respectively. These could be reduced or carried on to unsymmetrical bis(tertiary phosphines) in good yields. The complexes $1\text{-}\mu\text{-}PR^1\text{-}2\text{-}\mu\text{-}PR^2C_6H_4Fe_2(CO)_6$ ($R^1 = R^2 = t\text{-Bu}$; $R^1 = t\text{-Bu}$, $R^2 = Ph$; $R^1 = R^2 = 2,4,6\text{-}Me_3C_6H_2$) have been prepared in good yields and fully characterized.

Introduction

We have described a convenient synthesis of 1,2-bis(dimethoxyphosphoryl)benzene (**1**), which served as a precursor to 1,2-bis(phosphino)benzene (**2**).[1] We also reported that double deprotonation followed by alkylation gave **3a,b** and that **3a** could be transformed into **3c** by a

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