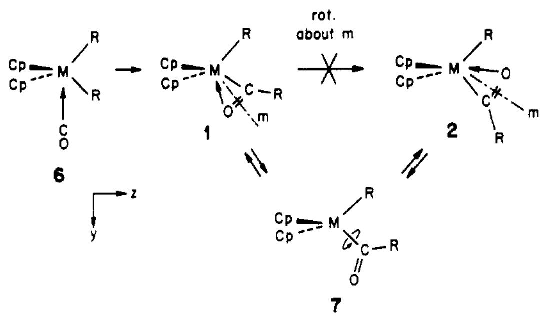
Scheme I



$Cp_2Ti(COCH_3)Cl$ are indeed of type **2**. The orientational preference is again a consequence of a better 3–4 overlap in **2**. Calculations for the two acyl orientations of $Cp_2U(COCH_3)Cl^{2+}$ produced potential surfaces similar to those in Figure 2. In the U case, **1** was found to be more stable than **2**, but only slightly. The energy difference amounts to merely 0.7 kcal/mol. Not surprisingly, the two isomers of $Cp^*_2M(CONR_2)Cl$ (M = Th, U) coexist either in solution or in the crystal.

The most striking feature of the potential energy surfaces in Figure 2 is the presence of *two* minima for the O-outside structure.[6] One is for the aforementioned η^2 type, and the other corresponds to an η^1 coordination appearing at $\alpha = 110°$ and $\beta = 105°$. This observation is important in considering a pathway for CO insertion into M–R bonds.

It has been predicted that the initial attack of CO on Cp_2MR_2 (M = Ti, Zr) occurs from the *y* direction as indicated in **6** in Scheme I.[7] Our detailed calculations on $Cp_2M(CH_3)_2$ + CO (M = Zr, U) have reached the same conclusion. The puzzling question then arose as to why only product **2** had been isolated for the Zr system, instead of the immediate product **1**. Subsequently a fleeting intermediate, very possibly **1**, has been noted in the reaction of $Cp_2Zr(p\text{-}CH_3C_6H_4)_2$ with CO, which then isomerizes irreversibly to the thermodynamically more stable structure **2**.[8] However, direct rotation of an η^2-acyl about the axis *m*, as shown in Scheme I, is not likely because strong bonds between ligands and a bent Cp_2M fragment are formed only when the coordination occurs in the yz plane.[7] In fact the calculated barrier to the rotation from **1** to **2** was as high as ~50 kcal/mol for the Zr complex. How then does the isomerization take place? We propose an alternative route via the η^1 O-outside intermediate **7**, which was found in our potential surface. The transformation of **1** to **7** is an easier process, requiring an activation energy of only 7.5 kcal/mol for $Cp_2Zr(COCH_3)(CH_3)$. The following step from **7** to **2** involves a rotation of η^1-acyl about the M–C single bond, which could be a free rotation if steric problems did not hamper it. The calculated rotational barrier from **7** amounts to 8.5 kcal/mol which, together with the calculated energy difference of 5 kcal between η^1 and η^2 O-outside minima, results in a computed barrier of 13.5 kcal for O-outside to O-inside rearrangement. The experimentally observed $\Delta G^\ddagger$ for the isomerization of $Cp_2Zr(COR)(R)$ ranges from 11.3 kcal/mol (R = CH_3) to 15.7 kcal/mol (R = *p*-tolyl, *p*-anisyl).[8]

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie (P.H. and P.S.) and to the National Science Foundation (R.H. and K.T.) for financial support. We also thank Dr. G. Erker for informative discussions.

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Mechanism of Olefin Insertion into Metal–Oxygen Bonds. Reaction of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Pt(CH_3)(OCH_3)$ with Tetrafluoroethylene[†]

Henry E. Bryndza

Central Research & Development Department
Experimental Station
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received September 17, 1984

Summary: The reaction of (DPPE)$Pt(CH_3)(OCH_3)$ [DPPE = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; bis(1,2-diphenylphosphino)ethane] (**1**) with tetrafluoroethylene (TFE) in THF-d_8 to form (DPPE)$Pt(CH_3)(CF_2CF_2OCH_3)$ (**2**) is first order in **1** and in TFE over a wide range of olefin concentrations ($\Delta H^\ddagger$ = 12.5 kcal/mol and $\Delta S^\ddagger$ = −32 eu). NMR measurements show no loss of ^{31}P or ^{195}Pt couplings to the methoxide protons in **1**, and **1** is insoluble in methanol. Thus methoxide does not dissociate from the starting material prior to forming **2**. Crossover experiments rule out a reaction mechanism involving charged intermediates arising from methoxide dissociation at any stage. At −80 °C the change in ^{19}F chemical shift of TFE was found to vary linearly with the quantity [**1**] [TFE], indicating that TFE and **1** interact, in preequilibrium fashion, to form a five-coordinate olefin complex as an intermediate in this reaction. Rate-limiting TFE insertion into the Pt–O bond of **1** follows at modest temperatures.

The sometimes severe conditions required for acid-catalyzed olefin hydration make a transition metal catalyzed route attractive. Of the steps necessary for catalytic olefin hydration,[1] only the coordination of an olefin to a hydroxo complex and the subsequent olefin insertion into its metal–oxygen bond are unknown.[2] The recently re-

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[†] Contribution No. 3550.

[1] A catalytic olefin hydration might involve (a) initial activation of an OH bond in water by a low-valent metal, (b) coordination of an olefin, followed by (c) olefin insertion into the M–O bond of the hydrido–hydroxo complex thus generated, and finally (d) the reductive elimination of product alcohol from a cis alkyl hydride to regenerate the low-valent metal catalyst. Step a is well precedented as is step d. (a) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027–38. (b) Yoshida, T.; Ueda, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 3941–3942. (c) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119–35. (d) Jones, R. F.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 58–9. (e) Halpern, J.; Abis, L.; Santi, R. *J. Organomet. Chem.* **1981**, *215*, 263–7. (f) Halpern, J.; Sen, A.; Abis, L. *J. Am. Chem. Soc.* **1978**, *100*, 2915–6. (g) Balazs, A. C.; Johnson, K. H.; Whitesides, G. M. Report TR-14; order #AD-A096 408; 1981. (h) Hill, R. H.; Puddephatt, R. J. *Inorg. Chim. Acta* **1981**, *54*, L277–L278. (i) Sostero, S.; Traverso, O.; Ros, R.; Michelin, R. A. *J. Organomet. Chem.* **1983**, *246*, 325–9.

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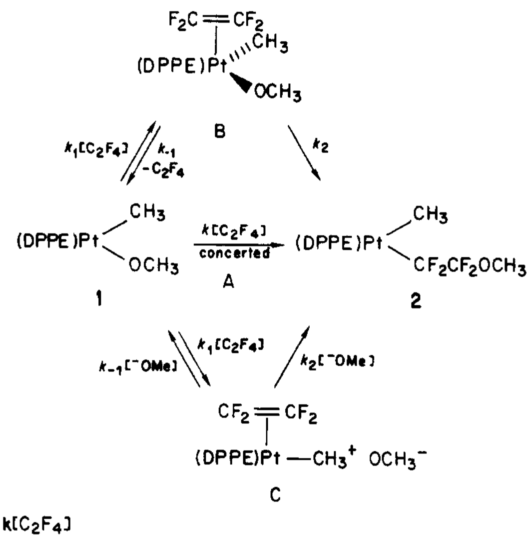
Scheme I



ported[3] synthesis of (DPPE)Pt(CH_3)(OCH_3) (1) and its unprecedented reaction with tetrafluoroethylene (TFE) (eq 1) to form 2 prompted our study of the reaction

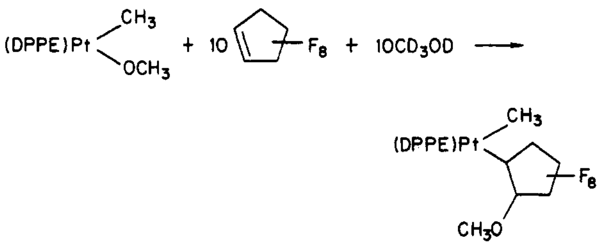
$$\underset{1}{(DPPE)PtCH_3(OCH_3)} + C_2F_4 \xrightarrow[THF\text{-}d_8]{25\,°C} \underset{2\ (>95\%\ yield)}{(DPPE)Pt(CH_3)(CF_2CF_2OCH_3)} \quad (1)$$

mechanism to determine if olefin insertions into metal-oxygen bonds are possible. This report indicates that TFE coordinates to 1 in a fast preequilibrium step and then inserts into the metal-oxygen bond to form 2.

The reaction in eq 1 can be followed by ^1H, ^{31}P, or ^{19}F NMR spectroscopy. Kinetics NMR measurements in THF-d_8 solution show the reaction is first order in 1[4] and first order in TFE over a wide range of olefin concentrations. In addition, ^{31}P and ^{195}Pt couplings to the methoxido protons of 1 do not change during this reaction, and methanol exchange studies[5] of 1 show the dissociation of methoxide (eq 2) is too slow to account for product formation. Activation parameters calculated from rates measured over a 45 °C range ($\Delta H^{\ddagger} = 12.5 \pm 0.1$ kcal/mol and $\Delta S^{\ddagger} = -32 \pm 5$ eu) are fully consistent with this conclusion and suggest the rate limiting step in this reaction is an associative one.

$$\underset{1}{(DPPE)PtCH_3(OCH_3)} \rightleftharpoons (DPPE)PtCH_3^+ + {}^-OCH_3 \quad (2)$$

While dissociative processes have been ruled out, three kinetically indistinguishable mechanisms still need evaluation. They are (Scheme I) (A) a concerted olefin insertion, (B) initial formation of a five-coordinate olefin complex followed by insertion, and (C) a mechanism involving the displacement of methoxide by olefin, followed by nucleophilic attack of free methoxide on the cationic olefin complex so generated. Crossover experiments (eq 3) in which 1 was combined with 10 equivalents each of CD_3OD and perfluorocyclopentene[6] show less than 8% OCD_3 groups in the product 3. These observations rule out mechanism C (or a hybrid in which 1 $\rightleftharpoons$ B $\rightleftharpoons$ C $\rightarrow$ 2) by showing methoxide never dissociates from platinum during this insertion reaction.



(3)

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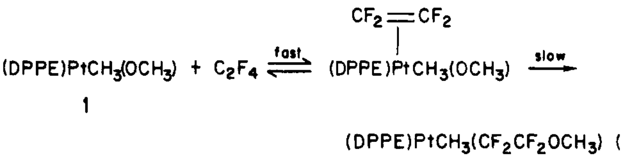
Since an inner-sphere insertion process describes the mechanism of these reactions, some ^{19}F NMR data becomes significant. When 1 and TFE were combined in an NMR tube, in THF-d_8, the change in chemical shift of TFE at −80 °C was found proportional to [1][TFE].[7] Under these conditions, no conversion to 2 was noted, though clearly there is a very facile interaction between TFE and 1. The mechanism consistent with these results is the coordinative process B. Under typical reaction conditions, a five-coordinate olefin complex is formed in rapid preequilibrium with starting materials; a rate-limiting olefin insertion into the metal-oxygen bond of 1 follows (eq 4).



$$\underset{1}{(DPPE)PtCH_3(OCH_3)} + C_2F_4 \overset{fast}{\rightleftharpoons} (DPPE)\overset{CF_2=CF_2}{Pt}CH_3(OCH_3) \xrightarrow{slow} \underset{2}{(DPPE)PtCH_3(CF_2CF_2OCH_3)} \quad (4)$$

This conclusion has several important and surprising ramifications. First of all, the hard base/soft acid complex 1 does not depend on dissociation of methoxide for reactivity. Secondly, the previously unknown olefin insertion into metal-oxygen bonds proceeds by the same mechanism as olefin insertions into metal-carbon and metal-hydrogen bonds and, in this case, is at least 3 orders of magnitude faster than the comparable insertion into the metal-carbon

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[2] The insertion of olefins into metal-oxygen bonds as a mechanistic step of the Wacker oxidation is still the subject of some debate. We are unaware of any simple olefin which has been shown to insert into metal-oxygen bonds, though examples of nucleophilic attack of oxy nucleophiles on coordinated olefins are well-known. Relevant articles to this controversy follow: (a) Stille, J. K.; Morgan, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 5135-5141. (b) Green, M.; Hancock, R. I. *J. Chem. Soc. A* **1967**, 2054-2057. (c) Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1968**, 464. (d) Stille, J. K.; Fox, D. B. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 157-161. (e) Green, M.; Sashan, J. K. K.; Al-Najjar, I. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1565-71. (f) Clark, H. C.; Goel, A. B.; Goel, S. *J. Organomet. Chem.* **1981**, *216*, C25-C28. (g) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959-60. (h) Stille, J. K.; Devakaruni, R. *J. Am. Chem. Soc.* **1978**, *100*, 1303-4. (i) Zaw, K.; Lautens, M.; Henry, P. M. *Organometallics* **1983**, *2*, 197-9. (j) Wan, W. K.; Zaw, K.; Henry, P. M. *J. Mol. Catal.* **1982**, *16*, 81-7. (k) Gragor, N.; Henry, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 681-2. (l) Henry, P. M. "Palladium-Catalyzed Oxidation of Hydrocarbons"; D. Reidel Publishing Co.: Dordrecht, Netherlands, 1980; Vol. 2.

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[4] Kinetics experiments were carried out in the probe of a Nicolet NT-360WB spectrometer at temperatures between 10 and 55 °C. Loss of starting material 1 was followed for at least 3 half-lives. Olefin concentrations range from 0.007 to 0.4 M with no indication of "saturation" behavior.

[5] Pseudo-first-order reaction of 1 with 10 equiv of CD_3OD shows $-d[1]/dt = k[1][CD_3OD]$; this result requires a nondissociative methanol exchange with the error in the intercept of a k_{obsd} vs. [CD_3OD] plot corresponding to the *maximum* rate of methoxide dissociation. This rate of dissociation is less than 10^{-7} s^{-1} at 25 °C in the solvent.

[6] Although methoxide dissociation from 1 is much slower than eq 1, overall methanol exchange is faster. However, perfluorocyclopentene reacts with 1 faster than methanol exchange though the ca. 8% crossover noted probably comes from CD_3OD exchange with 1.

[7] At [1] = 0.021 M and [C_2F_4] = 1.75 M, the $\Delta\delta$(^{19}F-TFE) = 84 Hz at −80 °C. Shift relative to 1.75 M C_2F_4 solution (which is 6 Hz shifted from the 0.04 M TFE solution). Precedent has been established for tetrafluoroethylene coordination to bis(phosphine)platinum(II) alkyl complexes prior to insertion of that olefin into platinum-carbon or platinum-hydrogen bonds. See: (a) Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1971**, *10*, 18-25. (b) Clark, H. C.; Puddephatt, R. J. *Inorg. Chem.* **1970**, *9*, 2670-2675.

bond of 1.[8] Finally, this reaction demonstrates that all steps in a hypothetical catalytic olefin hydration are possible. Investigations into the use of Pt(0) phosphine complexes as olefin hydration catalysts are in progress.

Acknowledgment. The technical competence of M. P. Stepro and the assistance of G. Kruppa and B. Dunn in the acquisition of NMR spectra have been appreciated.

Registry No. 1, 82405-05-8; 2, 91993-68-9; 3, 93503-83-4; C_2F_4, 18251-90-6; perfluorocyclopentene, 559-40-0; perdeuterated tetrahydrofuran, 1693-74-9.

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(8) Which is particularly interesting in light of calculations in: Bäckvall et al. *J. Am. Chem. Soc.* **1984**, *106*, 4369–4373 which suggest hydroxide ligands will always migrate more slowly to coordinated olefins (on four-coordinate Pd complexes) than alkyl ligands.

Hydride Transfer to Transition-Metal Carbonyls in the Gas Phase. The Heat of Formation of $(CO)_4FeCHO^-$

Kelley R. Lane, Larry Sallans, and Robert R. Squires*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47906

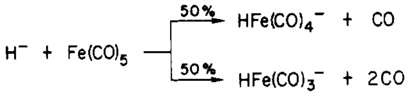
Received September 7, 1984

Summary: The hydride affinity of iron pentacarbonyl, $D[(CO)_4FeCO\text{–}H^-]$, has been determined from binary hydride-transfer reactions in the gas phase to be 56.1 ± 4.0 kcal/mol. From this, the heat of formation of the iron-formyl anion, $\Delta H_f[(CO)_4FeCHO^-,g] = -194.4 \pm 4.3$ kcal/mol, and the associated metal–acyl bond energies, $D[(CO)_4Fe^-\text{–}CHO] = 43.9 \pm 9.1$ kcal/mol and $D[(CO)_4Fe\text{–}CHO^-] = 101.1 \pm 6.1$ kcal/mol, have been derived. The direct reaction of hydride ion with $Fe(CO)_5$ occurs at 40.0% of the collision-limited rate and produces roughly equal amounts of $HFe(CO)_4^-$ and $HFe(CO)_3^-$ as products. The relationship of these data to metal–formyl reactivity in solution is discussed.

Transition-metal formyls and hydrides have received considerable attention over the last decade as key intermediates in the metal-catalyzed reduction of CO and CO_2 by H_2.[1,2] Model formyl complexes have been generated in solutions of the corresponding metal carbonyl and borohydride reagents and have been reported to function as hydride reducing agents in the presence of simple ketones, aldehydes, and other metal carbonyls.[3] While the synthesis and reactivity of metal formyls has been extensively investigated,[4] there are only scant thermochemical data available to guide the rational design off more effective formyl-based catalysts. Recently, a wealth of new thermodynamic data for transition-metal compounds has emerged from studies of organometallic ions in the gas phase.[5] In the course of our own studies of the gas-phase chemistry of anionic metal acyls related to homogeneous catalysis,[6] we have recently observed the simple iron-formyl ion, $(CO)_4FeCHO^-$, as a product of binary hydride-transfer reactions. In this note we report a determination of the hydride affinity of $Fe(CO)_5$ and a derivation of $\Delta H_f[(CO)_4FeCHO^-,g]$.

Our experiments have been carried out at 300 ± 2 K in a flowing afterglow apparatus that has been described in detail previously.[6] Hydride donor anions such as $C_6H_5\bar{C}HCH_3$, HCO_2^-, and $CH_3\bar{C}HCOCH_3$ are produced from proton-transfer reactions between an appropriate neutral precursor ($C_6H_5CH_2CH_3$, HCO_2H, and $CH_3CH_2COCH_3$, respectively) and NH_2^-, the latter being generated by electron impact on NH_3. A fast flow of helium buffer gas[7] carries these ions the length of a 100 cm × 7 cm i.d. flow reactor where they interact with $Fe(CO)_5$ added to the system through a moveable injector. The steady-state ion composition in the flow tube is continuously monitored by a quadrupole mass spectrometer located behind a small sampling orifice.

Before proceeding on to the results for hydride transfers, it is important to first consider the direct reaction of $Fe(CO)_5$ with hydride ion itself. Stable signals of H^- may be produced in the flow reactor from adding excess H_2 to NH_2^- and the ensuing proton transfer. An exceedingly rapid reaction with $Fe(CO)_5$ is observed which yields two hydridoiron carbonyl ions as primary products in roughly equal abundance (eq 1).[8]



$$H^- + Fe(CO)_5 \longrightarrow \begin{cases} \xrightarrow{50\%} HFe(CO)_4^- + CO \\ \xrightarrow{50\%} HFe(CO)_3^- + 2CO \end{cases} \tag{1}$$

The bimolecular rate coefficient for this reaction has been determined to be $(4.93 \pm 0.66) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} which indicates, when compared with the ion–molecule collision rate ($k_{Langevin} = 1.24 \times 10^{-8}$ cm^3 $molecule^{-1}$ s^{-1}),[9] that reaction is occurring on approximately every other encounter. Interestingly, we find that the $HFe(CO)_3^-$ ion undergoes secondary reactions with excess $Fe(CO)_5$ to produce the dinuclear hydrides $HFe_2(CO)_6^-$ and $HFe_2(CO)_7^-$ as well as a fast addition reaction with CO_2 to produce $HFe(CO)_3(CO_2)^-$.[10] In contrast, the 18-electron tetracarbonyl ion $HFe(CO)_4^-$ appears to be relatively inert toward either $Fe(CO)_5$ or CO_2. We have noted similar gas-phase reactivity patterns in other saturated (18 electron) vs. unsaturated (16-electron) $M(CO)_nL^-$ ions.[11]

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(7) Standard experimental conditions for our experiments are $P(He) = 0.40$ torr, $F(He) = 180$ STP cm^3 s^{-1}, $\bar{v} = 8970$ cm s^{-1}, and $T = 300 \pm 2$ K.

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