Communications to the Editor

β-Elimination from a Metal Acetyl Compound To Form Ketene and a Metal Hydride

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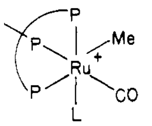
Received October 2, 1984

In recent years, studies of organometallic compounds containing chiral metal atoms have generally shed much light on organometallic reaction mechanisms.[1,2] In spite of considerable effort with chiral iron complexes of the type CpFeCOLR (L = neutral ligand; R = alkyl), however, knowledge of the stereochemistry, and hence of the mechanism(s), of the so-called "carbonyl insertion" reaction (eq 1) remains confused. Retention, inversion, and racemization at iron have all been observed, the stereochemistry of the products formed being dependent on the nature of the solvent and the presence of Lewis acids.[3-6]

$$\mathrm{CpFeCOLR} + \mathrm{L'} \rightarrow \mathrm{CpFeLL'(COR)} \qquad (1)$$

We have recently initiated studies of a novel series of chiral octahedral complexes exemplified by $[\mathrm{RuMe(CO)L(triphos)}]^+$ (**1**)



1, L = *t*-BuNC

(triphos = $\mathrm{MeC(CH_2PPh_2)_3}$). Compound **1** has been successfully resolved and its absolute configuration has been determined.[7] Attempts have been made to carbonylate **1** and a precursor, $[\mathrm{RuMe(CO)_2(triphos)}]^+$, in order to assess the stereochemical implications. Unfortunately, no acetyl species could be obtained, even at 95 °C (250 atm).

It was therefore decided to attempt to prepare an acetyl complex by oxidative addition of acetyl chloride to $\mathrm{Ru(CO)_2(triphos)}$, i.e.,

$$\mathrm{Ru(CO)_2(triphos)} + \mathrm{MeCOCl} \rightarrow \underset{\mathbf{2}}{[\mathrm{Ru(COMe)(CO)_2(triphos)}]\mathrm{Cl}} \qquad (2)$$

Although the similar oxidative addition of methyl iodide occurs readily,[7] reaction of acetyl chloride in several solvents gave only the new hydride $[\mathrm{RuH(CO)_2(triphos)}]\mathrm{Cl}$ (**3**),[8] in close to quantitative yields. Careful purification and drying of the reagents, solvents, and glassware ensured that **3** was not formed via the oxidative addition of adventitious HCl, which could occur readily.[7] Furthermore, reaction of $\mathrm{CD_3COCl}$ gave the ruthenium deuteride $[\mathrm{RuD(CO)_2(triphos)}]^+\mathrm{Cl}^-$,[9] suggesting that the reaction proceeds as in eq 3.

$$\mathrm{Ru(CO)_2(triphos)} + \mathrm{MeCOCl} \rightarrow \underset{\mathbf{3}}{[\mathrm{RuH(CO)_2(triphos)}]\mathrm{Cl}} + \mathrm{CH_2{=}C{=}O} \qquad (3)$$

The presence of ketene (bp -56 °C) was confirmed in a number of ways. Refluxing $\mathrm{Ru(CO)_2(triphos)}$ in neat acetyl chloride under a flow of nitrogen gave a gaseous product which was trapped, along with some acetyl chloride, at -196 °C. On warming, dissolution in methylene chloride, and rapid scanning of the IR spectrum, a band at 2140 $\mathrm{cm^{-1}}$ was observed, attributable to ketene.[10] On addition of ethanol, the band at 2140 $\mathrm{cm^{-1}}$ disappeared immediately (much more rapidly than the carbonyl peak of acetyl chloride), and there appeared the spectrum of ethyl acetate, the product expected from the reaction of ethanol with both acetyl chloride and ketene.[11]

Dissolution of the trapped gaseous products in $\mathrm{CDCl_3}$ at -60 °C gave a solution whose $^{13}\mathrm{C}$ NMR spectrum (-60 °C) exhibited, besides the resonance of acetyl chloride, resonances at 193.72 (s) and 2.70 ppm (t, J_{CH} = 177 Hz), attributable to the ketene carbonyl and methylene resonances, respectively.[12] Addition of $\mathrm{D_2O}$ to the solution resulted in the appearance of new $^{13}\mathrm{C}\{^1\mathrm{H}\}$ resonances, attributable to $\mathrm{CH_3CO_2D}$, at 176.42 (CO) and 20.40 ($\mathrm{CH_3}$) ppm. Superimposed on the latter was a 1:1:1 triplet centered at 20.24 ppm (J_{CD} = 19.9 Hz), the methyl carbon resonance of $\mathrm{CH_2DCO_2D}$, which is the product expected from the reaction of ketene with $\mathrm{D_2O}$.[11,13,14] In addition, the $^1\mathrm{H}$ NMR spectrum of the same solution exhibited a singlet at δ 2.10 and a 1:1:1 triplet (J_{HD} = 2.12 Hz) at δ 2.09, attributable to $\mathrm{CH_3CO_2D}$ and $\mathrm{CH_2DCO_2D}$, respectively.

Three mechanisms seem possible for the formation of ketene, direct dehydrohalogenation of acetyl chloride or acetyl complex **2** by $\mathrm{Ru(CO)_2(triphos)}$, a mild base,[15] or β-elimination from the acetyl complex **2**. The first two routes involve simple deprotonation steps and, if relevant here, might be expected to occur generally during the reactions of acid halides with low-valent metal complexes or carbonylate anions. Although such reactions provide common routes to acylmetal complexes,[16,17] a search of the literature found no report of formation of metal hydride byproducts. As tertiary amines are believed in any case to induce ketene formation from acid halides via formation of acylammonium salts,[18] we looked for evidence for **2** as an intermediate.

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[7] Hommeltoft, S. I.; Cameron, A. D.; Shackleton, T. A.; Fraser, M. E.; Fortier, S.; Baird, M. C. *J. Organomet. Chem.*, in press.

[8] $\nu_{\mathrm{CO}}(\mathrm{CH_2Cl_2})$ = 2010 (s), 2057 (vs) $\mathrm{cm^{-1}}$. Hydride chemical shift ($\mathrm{CDCl_3}$) = -6.75 ppm (d t, trans J_{PH} = 64 Hz, cis J_{PH} = 15 Hz).

[9] Deuteride resonance at -7.05 ppm (br d, trans $J_{\mathrm{PH}} \sim$ 11 Hz).

[10] Gaseous ketene absorbs at 2151 $\mathrm{cm^{-1}}$. Arendale, W. F.; Fletcher, W. H. *J. Chem. Phys.* **1957**, *26*, 793.

[11] Borrmann, D. In "Methoden der Organischen Chemie (Houben-Weyl)", 4th ed.; Georg Thieme Verlag: Stuttgart, West Germany, 1968; Band VII/4, Sauerstoff-Verbindungen II, Teil 4, p 53.

[12] Lit. ($\mathrm{CDCl_3}$, -60 °C) 194.0, 2.5 ppm (t, J_{CH} = 171.5 Hz). Firl, J.; Runge, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1974**, *29B*, 393.

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[15] $\mathrm{Ru(CO)_2(triphos)}$ is partially protonated by acetic acid, while its conjugate acid, **3**, is partially deprotonated by diethylamine, both in methylene chloride.

[16] See, for example: McClerverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 4096. Coffield, T. H.; Kozikowski, J.; Closson, R. D. *J. Org. Chem.* **1957**, *22*, 598. Hieber, W.; Braun, G.; Beck, W. *Chem. Ber.* **1960**, *93*, 901. King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1918. Cook, C. D.; Jauhal, G. S. *Can. J. Chem.* **1967**, *45*, 301. Bennett, M. A.; Charles, R.; Mitchell, T. R. B. *J. Am. Chem. Soc.* **1978**, *100*, 2737.

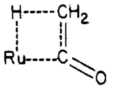
[17] Acetylmanganese compounds, for instance, appear to be stable with respect to deprotonation by alkoxide ions and amines. See: Calderazzo, F.; Noack, K. *J. Organomet. Chem.* **1965**, *4*, 250. Keblys, K. A.; Filbey, A. H. *J. Am. Chem. Soc.* **1960**, *82*, 4204. Kraihanzel, C. S.; Maples, P. K. *Inorg. Chem.* **1968**, *7*, 1806. Furthermore, $\mathrm{CpFe(CO)(PPh_3)COMe}$ is not deprotonated by bases weaker than *n*-butyllithium or lithium diisopropoxide; see: Aktogu, N.; Felkin, H.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1982**, 1303.

[18] Ward, R. S. In "The Chemistry of Ketenes, Allenes and Related Compounds"; Patai, S., Ed.; Wiley: New York, 1980; Part 1, p 223.

0002-7863/85/1507-2548$01.50/0

Monitoring by FTIR spectroscopy the reaction of equimolar amounts of $Ru(CO)_2$(triphos) ($\nu_{CO} = 1941, 1858\ cm^{-1}$) and acetyl chloride ($\nu_{CO} = 1803\ cm^{-1}$) in methylene chloride at room temperature resulted in observation of the smooth disappearance of the carbonyl stretching bands of the reactants and the smooth appearance to the two ν_{CO} of **3** (2057, 2010 cm^{-1}). Interestingly, a weak shoulder on the high-frequency side of the 2057-cm^{-1} band was observed to appear and remain throughout the reaction. Subtraction of the two ν_{CO} of **3** subsequently made possible the observation of two new, weak bands at 2085 and 2056 cm^{-1}. As the acetyl group is more electronegative than hydrogen, it seems reasonable to assign the weak bands to **2**, formed in a very low steady-state equilibrium concentration.

If these assignments are correct, the rate-determining step in the formation of ketene would be the conversion of **2** to products, a β-elimination reaction involving migration of hydrogen from carbon to ruthenium. A primary kinetic isotope effect might be expected, and accordingly a competition reaction was carried out between $Ru(CO)_2$(triphos) and a 2:1 mixture of CH_3COCl and CD_3COCl. The resulting ketenes were trapped as described above and treated with water, and the ratio of CH_3CO_2H to CD_2HCO_2H was determined mass spectrometrically. The ruthenium-containing products were also isolated, and the ratio of $[RuH(CO)_2(triphos)]^+$ to $[RuD(CO)_2(triphos)]^+$ was determined by ^1H NMR spectroscopy. The kinetic isotope effect obtained by these methods was 3.0 ± 1.0, certainly a primary isotope effect and consistent with a nonlinear C--H--Ru transition state[19] of the type expected for a β-elimination reaction, i.e.,



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Indeed, although not very precise, the measured kinetic isotope effect is similar to kinetic isotope effects reported for reactions involving β-elimination of olefins from alkyl compounds of cobalt (2.30 ± 0.05),[20] iridium (2.28 ± 0.20),[21] and palladium (1.4 ± 0.1).[22] Again, a nonlinear C--H--M transition state is favored.[23]

Although elimination of ketenes from acetyl complexes appears to be unprecedented, there have been two reports of ketene insertions into metal–hydrogen bonds,[24,25] i.e.,

$$HMn(CO)_5 + CH_2{=}C{=}O \rightarrow MeCOMn(CO)_5$$

$$HCo(CO)_4 + R_1R_2C{=}C{=}O \rightarrow R_1R_2CHCOCO(CO)_4 \qquad (4)$$

$$R_1, R_2 = H, Me, Et$$

In addition, we note a crystal structure of an acetyl compound, $Mo(COMe)(S_2CNMe_2)(CO)(PMe_3)_2$, in which there is a strong, attractive interaction between the metal atom and one of the hydrogen atoms of the acetyl group.[26] Although it has been suggested[26] that the structure provides a possible model for the transition state (or intermediate) of the migratory insertion of carbon monoxide into metal–carbon bonds, the structure possibly provides a model for the elimination reaction described above. Similar metal–β-CH interactions of alkylmetal compounds, reported in the literature, have been cited as models of the transition state for olefin β-elimination reactions.[27-29]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council for financial support, Queen's University and the NATO Science Fellowship Program for scholarships awarded to S.I.H., and Johnson Matthey and the International Nickel Co. of Canada for loans of ruthenium trichloride. We are also much indebted to J. A. Stone for running the mass spectra.

Registry No. 3, 95123-22-1; $Ru(CO)_2$(triphos), 37843-33-7; $CH_3C(O)Cl$, 75-36-5; $CD_3C(O)Cl$, 19259-90-6; $[RuD(CO)_2(triphos)]Cl$, 95123-23-2; $CH_2{=}CO$, 463-51-4; D_2, 7782-39-0.

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[29] As suggested by a referee, a transition state as in **4** requires a vacant site on the ruthenium. We doubt that phosphorus atom dissociation occurs during elimination and suggest that a CO dissociates but does not escape from the solvent cage before the ketene dissociates. Alternatively, reactions 3 and 4 may occur via radical processes as, apparently, can "insertion" reactions of dienes with some metal hydrides.[30] The significance of a primary kinetic isotope effect in the reverse reactions would be unclear.

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Mechanism of Cytochrome P-450 Catalysis. Mechanism of N-Dealkylation and Amine Oxide Deoxygenation

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Received July 13, 1984

The cytochrome P-450 enzymes, which catalyze a variety of oxidative and reductive transformations, have received considerable attention with regard to their catalytic mechanisms.[1] These studies suggest that carbinolamine formation is the penultimate step in the mechanism for N-dealkylation, a representative oxidative heteroatom dealkylation process. The oxygen atom in the carbinolamine is derived from O_2;[2] however, the sequence of events leading to the carbinolamine intermediate has not been completely resolved. Relatively small *intermolecular* deuterium isotope effects have been observed for N-dealkylation indicating that breaking the α-carbon–hydrogen bond is not rate determining in the catalytic mechanism.[3-6] Moderate *intramolecular* isotope effects

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