Oxidative Addition and Reversible Dehydrohalogenation of α,ω-Alkanedioyl Dichlorides. Formation of a Metallo-Enol Lactone Complex via Intramolecular Cyclization

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Summary: Controlled oxidative addition of one end of an α,ω-alkanedioyl dichloride to Vaska's complex, $(Ph_3P)_2Ir(CO)Cl$, is reported, giving an Ir(III) acyl complex bearing pendant acid chloride functionality. This complex undergoes a thermal dehydrohalogenation and intramolecular cyclization to afford an interesting metallo-enol lactone complex. The cyclization is reversed quantitatively by treatment with an excess of anhydrous hydrochloric acid and appears to proceed via an intermediate cationic Ir(III) carbene complex.

For a project directed toward the synthesis of novel oxygen-substituted metallacyclic complexes, we have been exploring the potential for controlling the reactivity of α,ω-alkanedioyl dichlorides toward low-valent late transition metal complexes. For this purpose, selective oxidative addition of one end of the bis(acid chloride) was required, to be followed by decarbonylation of the resultant metal acyl complex without affecting the pendant acid chloride functionality. Reactions of nucleophilic transition-metal complexes with various alkanedioyl dichlorides have been previously reported, typically leading to the formation of doubly metalated bis(acyl) products.[2] An attempt to form heterobimetallic bridging bis(acyl) complexes by controlled monometalation using anionic molybdenum and tungsten complexes was very recently reported, and although displacement at only one end of the bis(acid chloride) was observed, a base-assisted intramolecular cyclization followed, giving an interesting metallo-enol lactone complex.[3,4]

Herein we report successful controlled monometalation of an alkanedioyl dichloride and a similar, but thermally induced, intramolecular cyclization process, which proved to be reversible. The alkanedioyl dichloride selected for this study was diglycolyl dichloride (**1**),[5] the oxygen substituted analogue of glutaryl dichloride. Treatment of diglycolyl dichloride with an equimolar amount of Vaska's complex in benzene solution at room temperature gave the desired mono acyl complex **2** in 75% yield after direct crystallization from the reaction mixture by addition of pentane (Scheme I).[6] No double oxidative addition product was observed. The infrared spectrum of this material was characteristic: three strong carbonyl bands at 2050, 1800, and 1635 cm^{-1} for the metal carbonyl, acid chloride, and metal acyl stretches, respectively. The stereochemistry of acyl complex **2** follows from that observed for simple oxidative addition of acid chlorides to Vaska's complex,[7] and the metal acyl stretching frequency indicates significant electron donation from the metal, as observed for related Ir(III) acyl complexes.[7]

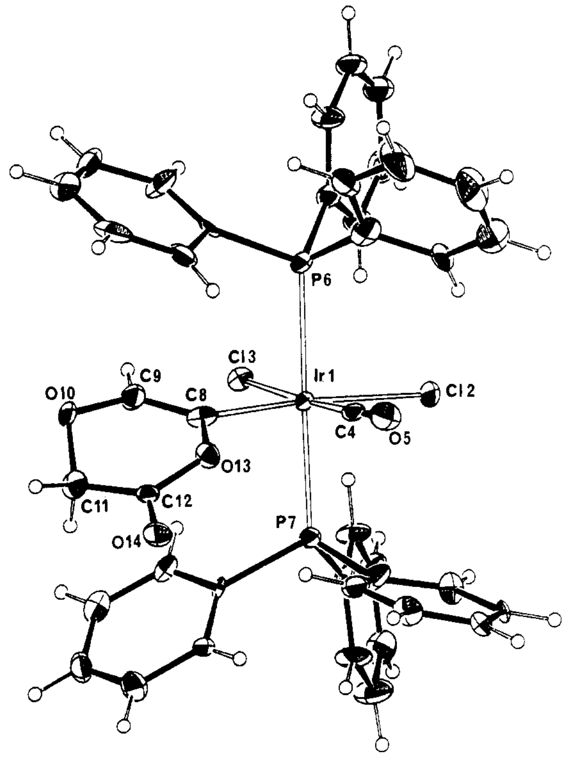
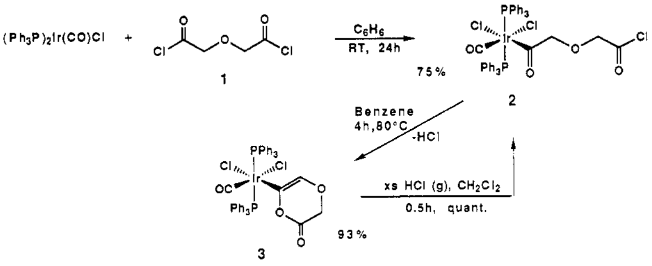


Figure 1. ORTEP drawing of complex **3**. Selected bond distances (Å): Ir(1)–Cl(2), 2.459 (4); Ir(1)–Cl(3), 2.391 (4); Ir(1)–P(6), 2.398 (4); Ir(1)–P(7), 2.400 (4); Ir(1)–C(4), 1.845 (23); Ir(1)–C(8), 2.041 (15); O(13)–C(8), 1.432 (18); C(8)–C(9), 1.312 (22); O(10)–C(9), 1.385 (19); O(10)–C(11), 1.436 (19); C(11)–C(12), 1.475 (23); O(13)–C(12), 1.351 (18); O(14)–C(12), 1.191 (18). Selected bond angles (deg): Cl(2)–Ir(1)–Cl(3), 92.09 (14); Cl(2)–Ir(1)–P(6), 91.95 (13); Cl(2)–Ir(1)–P(7), 87.80 (13); Cl(2)–Ir(1)–C(4), 88.8 (5); Cl(2)–Ir(1)–C(8), 175.0 (4); Cl(3)–Ir(1)–P(6), 87.42 (15); Cl(3)–Ir(1)–P(7), 94.20 (14); Cl(3)–Ir(1)–C(4), 176.6 (5); Cl(3)–Ir(1)–C(8), 88.8 (5); P(6)–Ir(1)–P(7), 178.37 (16); Ir(1)–C(8)–O(13), 112.7 (10); Ir(1)–C(8)–C(9), 130.9 (12).

Scheme I



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[1] Du Pont Young Faculty Awardee, 1988–1989. Union Carbide Innovation Recognition Program Awardee, 1989.

[2] (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *7*, 311. (b) Moss, J. R. *J. Organomet. Chem.* **1982**, *231*, 229. (c) Kao, S. C.; Thiel, C. H.; Petit, R. *Organometallics* **1983**, *2*, 914. (d) Schulze, W.; Hartl, H.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 185.

[3] Wong, A.; Morgan, R. L., II; Golder, J. M.; Quimbita, G. E.; Pawlick, R. V. *Organometallics* **1989**, *8*, 844.

[4] A similar intramolecular cyclization apparently occurs on treatment of $Na_2Fe(CO)_4$ with phthaloyl dichloride, resulting in an unstable carbene intermediate: Mitsudo, T.; Watanabe, Y.; Tanaka, M.; Yamamoto, K.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1972**, 305.

[5] Dietrich, B.; Lehn, M.; Sauvage, J. P.; Blanzat, J. *Tetrahedron* **1973**, *29*, 1629. Mass, G. E.; Bradshaw, J. S.; Izatt, R. M.; Christensen, J. J. *J. Org. Chem.* **1977**, *42*, 3937.

[6] Spectroscopic data for complex **2**: mp >265 °C (sealed tube); IR (KBr): ν_{CO} 2050, 1800, 1635 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 2.78 (s, 2 H), 3.45 (s, 2 H), 7.45 (m, 18 H), 7.90 (m, 12 H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 75.7, 81.5, 128.6 (t, J_{PC} = 5.2 Hz), 129.2 (t, J_{PC} = 29.3 Hz), 131.6, 135.3 (t, J_{PC} = 4.4 Hz), 159.0 (t, J_{PC} = 3.3 Hz), 171.3, 205.2. Anal. Calcd for $C_{41}H_{34}O_4P_2Cl_3Ir$: C, 51.77; H, 3.59. Found: C, 51.89; H, 3.72.

[7] Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Organomet. Chem.* **1969**, *20*, 161. Kubota, M.; Blake, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 1368. See also: Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 1128.

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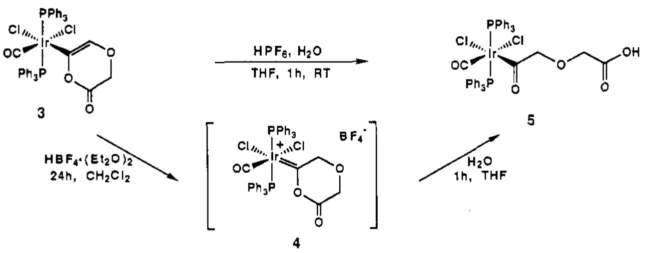
Scheme II



Attempted decarbonylation of complex **2** by warming in toluene under nitrogen led instead to the loss of 1 equiv of HCl and an intramolecular cyclization to the metallo-enol lactone complex **3** (Scheme I).[8] This material was obtained in 93% yield after crystallization from the reaction mixture on addition of pentane.[9] The metal acyl and acid chloride bands in the infrared were replaced by a single broad absorbance at 1735 cm^{-1}, and the ^1H NMR spectrum revealed an olefin proton at 4.99 ppm, coupled weakly and equivalently to two phosphorus nuclei. While the remaining spectral data[9] were fully consistent with the enol lactone formulation, confirmation of the structure was obtained by X-ray crystallography.[10] The molecular geometry and partial atom labeling scheme are given in Figure 1, along with selected bond distances and angles. The structure is unremarkable, minimally distorted from idealized octahedral geometry.

Interestingly, treatment of cyclized complex **3** in CH_2Cl_2 with an excess of dry HCl in a sealed vessel returned ring-opened complex **2** quantitatively (Scheme I). No protolytic loss of the organic ligand is observed. In fact, thermolysis of a CD_2Cl_2 solution of acyl complex **2** in a sealed NMR tube at 90 °C gives 91–95% conversion to cyclized complex **3**, which upon cooling to room temperature reverts back to predominantly complex **2**. Several cyclization/ring opening cycles can be conducted without appreciable decomposition of the sample.

Mechanistically, the reaction appears straightforward: nucleophilic attack on the electrophilic acid chloride carbonyl by the relatively electron-rich metal acyl. This postulate is consistent with the low-energy acyl infrared band, indicating significant electron donation from the metal despite its relatively high oxidation state. This leads to a hypothetical cationic iridium (III) carbene intermediate, which suffers proton loss to the weakly basic chloride ion. While such an intermediate is not observed in the thermal conversion of complex **2** to **3**, reaction of complex **3** with 1 equiv of anhydrous $HBF_4{\cdot}(Et_2O)_2$ gives an extremely hygroscopic complex which we have tentatively assigned to be carbene complex **4** (Scheme II).[11] ^1H NMR (CD_2Cl_2) analysis of this material shows two equal intensity nonaromatic signals, both broad singlets (3.04 and 2.16 ppm). Although this complex is as yet incompletely characterized, it readily undergoes hydrolysis to the open-chain acyl carboxylic acid complex **5** on treatment with water.[12] Identical material is isolated both from the reaction of the metallo-enol lactone complex directly on addition of aqueous acid in THF and from hydrolysis of complex **2**.

Complex **5** displays three carbonyl bands in the solid-state infrared spectrum, but a signal for the carboxylic acid proton was observed only in the ^1H HMR spectrum of a highly purified sample. The carboxylic acid carbonyl absorption is broad and centered at 1755 cm^{-1}, much closer in energy to typical values for monomeric species than to the normally observed carboxylic acid dimers. The OH out-of-plane bending mode expected at 920 cm^{-1}, also characteristic of the normal carboxylic acid dimer,[13] is notably absent, but the OH stretch is extremely broad, indicative of strong hydrogen bonding. Additionally, the metal acyl absorption for this material is observed at 1600 cm^{-1}, 35 cm^{-1} lower in energy than in acid halide complex **2**. Taken together, these data are suggestive of strong intramolecular hydrogen bonding between the metal acyl carbonyl and the hydroxy proton in this complex, leaving the carboxylic acid carbonyl absorption largely unaffected by hydrogen-bonding interactions.[14] A structural analysis is required to confirm this hypothesis.

In summary, controlled monooxidative addition of an α,ω-alkanedioyl dichloride has been observed, as well as a reversible intramolecular cyclization reaction to an interesting metallo-enol lactone complex. This reaction proceeds in the absence of base; indeed, attempted base-induced cyclization of complex **2** with either NaH or $NaN(SiMe_3)_2$ was not straightforward. Full characterization of the apparent intermediate carbene complex, and investigation of analogous all-carbon systems and corresponding intermolecular reactions is underway.

Acknowledgment. We thank Dr. John Huffman for the X-ray crystal structure determination. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Supplementary Material Available: Details of the data collection and structure solution, tables of atomic positional and thermal parameters, and complete bond distance and angle data (17 pages); a listing of F_o vs F_c (11 pages). Ordering information is given on any current masthead page.

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(8) The desired decarbonylated product is, however, readily available by an alternative synthesis, which will be reported separately. Zizelman, P. M.; Stryker, J. M., unpublished results.

(9) Spectroscopic data for complex **3**: mp 260–265 °C (sealed tube, dec); IR (KBr): ν_{CO} 2040, 1735 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 3.17 (s, 2 H), 4.99 (t, J_{PH} = 1.7 Hz, 1 H), 7.45 (m, 18 H), 7.90 (m, 12 H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 62.8, 117.5 (t, J_{PC} = 8.1 Hz), 128.0 (t, J_{PC} = 7.4 Hz), 128.8 (t, J_{PC} = 28.7 Hz), 131.2, 135.1, 158.6 (t, J_{PC} = 8.7 Hz), 164.4; $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2) δ −14.0. Anal. Calcd for $C_{41}H_{33}O_4P_2Cl_2Ir$: C, 53.88; H, 3.64. Found: C, 53.83; H, 3.85.

(10) Diffractable crystals were obtained by vapor diffusion of pentane into a methylene chloride solution. X-ray crystallography was carried out by Dr. John C. Huffman at the Indiana University Department of Chemistry Molecular Structure Center. Crystal data for complex **3**: $IrC_{41}H_{33}O_4P_2Cl_2$; space group $P2_1/c$; cell dimensions (at −155 °C) a = 11.911 (3), b = 17.498 (5), c = 18.080 (6) Å, β = 104.95 (1)°; Z (molecules/cell) = 4; V = 3640.71 $Å^3$; d(calcd) = 1.669; wavelength = 0.710 69 Å; linear absorption coefficient = 39.240 cm^{-1}; max absorptn = 0.5020, min absorptn = 0.6990. The structure was solved by using a combination of direct methods and Fourier techniques and was refined to final residuals $R(F)$ = 0.0644 and $R_w(F)$ = 0.0631 for 3953 independent reflections ($F > 3.00\sigma(F)$) of 4767 unique intensities collected in the range 6.0° $\leq 2\theta \leq$ 45.0°. Details of the data collection and structure solution, tables of atomic positional and thermal parameters, complete bond distance and angle data, and a listing of F_o vs F_c are included as supplementary information or may be obtained directly from the Molecular Structure Center. Request report No. 86117.

(11) The synthesis of cationic carbene complexes via protonation of σ-vinyl complexes is well-precedented: see, Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3761. Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119 and references therein.

(12) Spectroscopic data for complex **5**: mp >260 °C (sealed tube, dec); IR (KBr) ν_{CO} 2060, 1755, 1600 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 2.85 (s, 2 H), 2.89 (s, 2 H), 7.45 (m, 18 H), 7.89 (m, 12 H), 11.26 (br s, 1 H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 71.4, 85.5, 128.7 (t, J_{PC} = 3.6 Hz), 129.0 (t, J_{PC} = 28.5 Hz), 131.8, 135.3, (t, J_{PC} = 4.5 Hz), 158.8 (t, J_{PC} = 7.1 Hz), 171.7, 215.6. Although this complex is easily obtained as single crystals which are pure and free of residual solvents by spectroscopic analysis, we have been unable to obtain satisfactory data from elemental analysis.

(13) Conley, R. T. *Infrared Spectroscopy*, 2nd ed.; Allyn and Bacon: Boston, 1972; pp 160–163.

(14) These data are in contrast to that reported for $Cp(CO)_3W{-}CO(CH_2)_3CO_2H$, which displays a carboxylic acid infrared band at 1718 cm^{-1}. See ref 3.