Oxidative addition/decarbonylation of .alpha.,.omega.-alkanedioyl dichlorides. Metallacycle formation via intramolecular reductive cyclization of a pendant acid chloride using samarium(II) iodide

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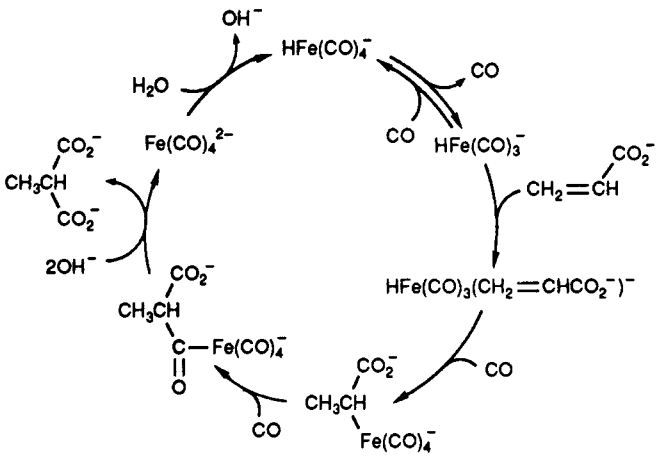
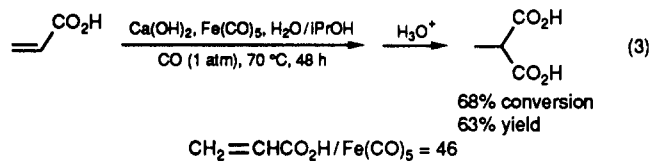
Organometallics, **1990**, 9 (6), 1713-1715• DOI: 10.1021/om00156a004 • Publication Date (Web): 01 May 2002

Scheme I



in an increase of the reaction rate (runs 5 and 6), which suggests that the acrylate moiety is involved in the rate-determining step of the reaction. Finally, iPrOH proved to be an even more efficient cosolvent than tBuOH (run 7, eq 3).



(3)

A simple catalytic scheme can be proposed (Scheme I) on the basis of the following observations.

(i) The reaction of eq 3 was quite inhibited when carried out under 20 bar of carbon monoxide pressure. This result suggested that the dissociative process $HFe(CO)_4^- \rightarrow HFe(CO)_3^- + CO$, previously proposed by several authors, was occurring.[7,8,22]

(ii) A stoichiometric reaction conducted on a 1.4-mmol potassium acrylate scale was monitored by quenching small aliquots with hydrochloric acid. The reaction never led to significant amounts of propionic acid (HPLC analysis), thus indicating that the concentration of the alkylferrate 4 was low throughout the reaction and that the rate-determining step is the formation of 4 from 1 and potassium acrylate. This hypothesis is supported by the fact that the reaction rate does depend on the acrylate concentration (vide supra).

(iii) Monitoring the reaction of eq 4 by IR analysis indicated that $HFe(CO)_4^-$ was the only detectable iron carbonyl species and that its concentration was almost constant throughout the reaction.

In summary, we have found the first catalytic hydrocarboxylation of acrylic acid into methylmalonic acid. The full regioselectivity and the mildness of reaction conditions must be emphasized. Work is in progress to develop further applications of this catalytic system.

Acknowledgment. We wish to thank Rhône-Poulenc for a studentship to E.P. and for financial support. Fruitful discussions with P. Leconte, R. Perron, and L. Krumenacker are gratefully acknowledged.

Registry No. $KHFe(CO)_4$, 17857-24-8; potassium acrylate, 10192-85-5; methylmalonic acid, 516-05-2; propionic acid, 79-09-4; iron pentacarbonyl, 13463-40-6; acrylic acid, 79-10-7.

(22) Wada, F.; Matsuda, T. *J. Organomet. Chem.* **1973**, *61*, 365.
(23) Eisenbraun, E. J.; Morris, R. N.; Adolphen, G. *J. Chem. Educ.* **1970**, 710.

Oxidative Addition/Decarbonylation of α,ω-Alkanedioyl Dichlorides. Metallacycle Formation via Intramolecular Reductive Cyclization of a Pendant Acid Chloride with Samarium(II) Iodide

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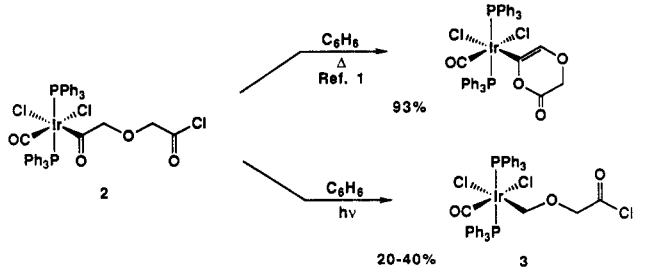
Received January 9, 1990

Summary: Controlled oxidative addition and decarbonylation at one end of α,ω-alkanedioyl dichlorides is reported with $(Ph_3P)_2Ir(N_2)Cl$, giving Ir(III) alkyl complexes bearing a pendant acid chloride functionality. The use of the dinitrogen complex enables suppression of competitive intramolecular lactonization processes. Use of 2 equiv of samarium(II) diiodide uniquely promotes intramolecular reductive cyclometalation of one of these complexes, forming a cyclic acyl complex. This cyclization is highly sensitive to both electronic factors in the substrate and the nature and stoichiometry of the reducing agent.

We recently reported the controlled oxidative addition of one end of diglycolyl dichloride (1) to Vaska's complex, giving the monometalated acyl complex **2**, free from competitive double metalation (Scheme I).[1] Decarbonylation

Scheme I



of this complex was anticipated to provide a substituted alkyl ligand bearing pendant acid chloride functionality, required as a precursor to novel oxygen-substituted metallacycle complexes. Attempted thermal decarbonylation of complex **2** instead resulted in an intramolecular cyclization of the pendant acid chloride onto the acyl functionality, giving an interesting but undesired metallo–enol lactone complex.[2] In this communication, we describe a

(1) Zizelman, P. M.; Stryker, J. M. *Organometallics* **1989**, *8*, 2075.

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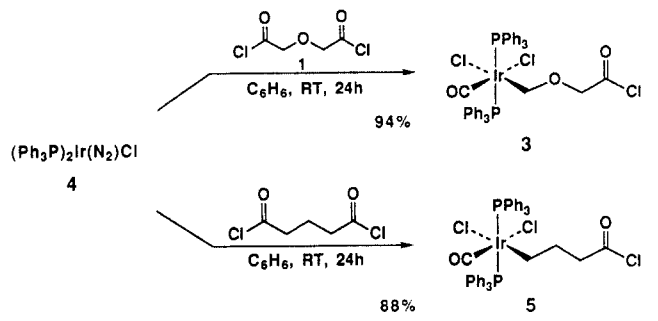
Scheme II



general procedure for accomplishing the desired decarbonylation selectively and address the question of metallacycle formation by intramolecular reductive coupling of the pendant acid chloride complex.

Suppression of the dehydrohalogenation/lactonization reactivity requires labilization of a ligand from the metal center at or below room temperature. Photolysis of the acyl complex[3] at room temperature (0.5 h, 450-W Hanovia lamp, Pyrex filter, C_6H_6) indeed gave the desired decarbonylated complex **3** in low to moderate yield (Scheme I), accompanied by substantial formation of Vaska's complex and other, unidentified byproducts. Although this photochemical activation was promising, an alternative strategy incorporating a more labile ligand into the starting material appeared more promising. The readily available dinitrogen complex $(Ph_3P)_2Ir(N_2)Cl$ (**4**),[4] previously demonstrated to undergo mild sequential oxidative addition and decarbonylation of acid chlorides,[5] thus became the focus of our investigation.

Treatment of dinitrogen complex **4** with diglycolyl dichloride (**1**) in benzene at room temperature led to gas evolution and development of a deep orange-red color characteristic of the expected five-coordinate Ir(III) acyl intermediate (Scheme II).[5,6] The solution bleached to pale yellow over 24 h and gave pure crystalline decarbonylated complex **3** as a benzene solvate in 94% isolated yield by concentration and addition of pentane.[7] The structural assignment is supported by infrared absorptions at 2040 and 1790 cm^{-1} for the metal carbonyl and acid chloride functionalities and the upfield chemical shift and broadening of the α-carbon resonance (δ 56.4) compared to that observed for acyl complex (**2** (δ 75.7).[1] The remaining methylene carbon resonance is relatively unperturbed by the decarbonylation. In the ^1H NMR spectrum, the resonance for the α-methylene protons exhibits the expected coupling due to the equivalent phosphine ligands, while the other methylene resonance appears at significantly higher field than expected, an anisotropic shielding effect previously noted for Ir(III) alkyl complexes bearing mutually trans aromatic phosphine ligands.[8] While the stereochemistry of this material has not been unambiguously determined, it has been assigned as indicated on the basis of considerable literature precedent.[5,8,9] To test the generality of this decarbonylation procedure, glutaryl dichloride was added to dinitrogen complex **4** and similarly gave pendant acid chloride complex **5** in 88% isolated yield after direct crystallization from the reaction mixture (Scheme II).[10] The spectroscopy of this material was quite similar to that observed for the oxygenated complex **3**, with the exception of the chemical shifts and more complicated coupling patterns expected for the all-carbon side chain.

Attempts to induce reductive cyclometalation of the pendant acid chloride complexes were much less straightforward. Superficially similar cyclizations of pendant haloalkyl functionality have been described for many transition-metal halide complexes, resulting in metallacycle complexes of several ring sizes.[11] These reactions almost certainly proceed by facile reduction at the metal–halide bond, followed by oxidative addition at the carbon–halogen bond on the pendant alkyl. No such cyclometalation has been reported with any other organic functionality at the ligand terminus. In the case of the more easily reduced pendant acid chloride, the initial site of reduction is considerably more ambiguous, and treatment of complex **3** with standard reducing agents (Na/Hg, Li, Mg, Na/K, sodium naphthalenide, Zn, Al/Hg) under a variety of conditions failed to yield any product retaining the organic ligand.

The Lewis acidic one-electron reducing agent SmI_2[12] has recently seen extensive development in the area of reductive coupling in organic synthesis,[12a,13] including reactions involving the acid chloride functionality.[14] In the case of pendant acid chloride complex **3**, rapid addition of 2 equiv of SmI_2 (0.04 M in THF) to a solution of **3** in anhydrous THF at room temperature gave the desired metallacyclic acyl complex **6**[15] in 71% yield after evaporation of the volatiles, trituration of the residue with benzene, and purification of the crude product by flash chromatography[16] under an inert atmosphere (eq 1).[17] The presence of the acyl functionality was confirmed by both

(2) Related examples: Mitsudo, T.; Watanabe, Y.; Tanaka, M.; Yamamoto, K.; Takegami, Y. *Bull. Chem. Soc. Jpn.* **1972**, 305. Wong, A.; Morgan, R. L., II; Golder, J. M.; Quimbita, G. E.; Pawlick, R. V. *Organometallics* **1989**, *8*, 844.

(3) See: Wojcicki, A. A. *Adv. Organomet. Chem.* **1973**, *11*, 87 and references therein.

(4) Collman, J. P.; Kubota, M.; Vastine, F. D.; Sun, J. Y.; Kang, J. W. *J. Am. Chem. Soc.* **1968**, *90*, 5430. Collman, J. P.; Hoffman, N. W.; Hosking, J. W. *Inorg. Synth.* **1970**, *12*, 8.

(5) Kubota, M.; Blake, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 1368. Kubota, M.; Blake, D. M.; Smith, S. A. *Inorg. Chem.* **1971**, *10*, 1430.

(6) See: Blake, D. M.; Vinson, A.; Dye, R. *J. Organomet. Chem.* **1980**, *204*, 257 and references therein.

(7) Spectroscopic data for complex **3**: IR (KBr) ν_{CO} 2040, 1790 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 3.23 (s, 2 H), 4.23 (t, J_{PH} = 4.6 Hz, 2 H), 7.50 (m, 18 H), 8.05 (m, 12 H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 56.4 (br s), 78.4, 128.4 (virtual t, J_{PC}= 7.9 Hz), 129.9 (virtual t, J_{PC} = 29.3 Hz), 131.2 (m), 135.0 (m), 160.3 (t, J_{PC} = 8.4 Hz), 171.6. Anal. Calcd for $C_{40}H_{34}Cl_3O_3P_2Ir \cdot C_6H_6$: C, 55.17; H, 4.02. Found: C, 54.95; H, 4.05.

(8) Bennett, M. A.; Jeffery, J. C. *Inorg. Chem.* **1980**, *19*, 3763. Bennett, M. A.; Charles, R.; Mitchell, T. R. B. *J. Am. Chem. Soc.* **1978**, *100*, 2737.

(9) Glyde, R. W.; Mawby, R. J. *Inorg. Chim. Acta* **1971**, *5*, 317.

(10) Spectroscopic data for complex **5**: IR (KBr) ν_{CO} 2030, 1800 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 1.12 (m, 2 H), 1.33 (m, 2 H), 1.80 (m, 2 H), 7.45 (m, 18 H), 8.02 (m, 12 H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 10.9 (br s), 32.0, 50.0, 128.5 (virtual t, J_{PC} = 3.3 Hz), 129.4 (virtual t, J_{PC} = 28.4 Hz), 131.3, 135.2 (virtual t, J_{PC} = 4.1 Hz), 162.9 (t, J_{PC} = 8.6 Hz), 172.6. Anal. Calcd for $C_{41}H_{36}Cl_3O_2P_2Ir$: C, 53.45; H, 3.94. Found: C, 52.99; H, 4.06.

(11) (a) Mickiewicz, M.; Wainwright, K. P.; Wild, S. B. *J. Chem. Soc., Dalton Trans* **1976**, 262. (b) Lindner, E.; Neese, P.; Hiller, W.; Fawzi, R. *Organometallics* **1986**, *5*, 2030 and references therein.

(12) (a) Review: Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573. (b) Namy, J. L.; Girard, P.; Kagan, H. B. *Nouv. J. Chim.* **1977**, *1*, 5. (c) Girard, P.; Kagan, H. B.; Namy, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

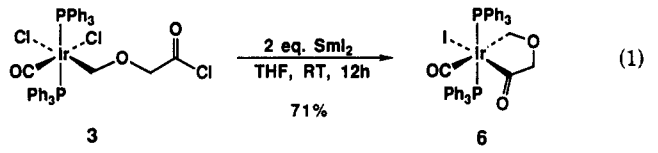
(13) Otsubo, K.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986**, *27*, 5763. Imamoto, T.; Takiyama, N. *Tetrahedron Lett.* **1987**, *28*, 1307. Molander, G. A.; Kenny, C. *J. Org. Chem.* **1988**, *53*, 2132.

(14) (a) Girard, P.; Couffignal, R.; Kagan, H. B. *Tetrahedron Lett.* **1981**, *22*, 3959. (b) Souppe, J.; Namy, J. L.; Kagan, H. B. *Tetrahedron Lett.* **1984**, *25*, 2869. (c) Ghiringhelli, D. *Tetrahedron Lett.* **1983**, *24*, 287.

(15) Spectroscopic data for complex **6**: IR (KBr) ν_{CO} 2020, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.84 (s, 2 H), 5.35 (t, J_{PH} = 7.9 Hz, 2 H), 7.40 (m, 18 H), 7.70 (m, 12 H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 67.4 (t, J_{PC} = 5.6 Hz), 81.0, 127.9 (m), 129.9 (virtual t, J_{PC} = 30.0 Hz), 131.0, 134.9 (m), 158.7 (t, J_{PC} = 7.4 Hz), 229.5 (br). Anal. Calcd for $C_4H_{34}IO_3P_2Ir$: C, 50.91; H, 3.63. Found: C, 51.35; H, 3,86.

(16) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

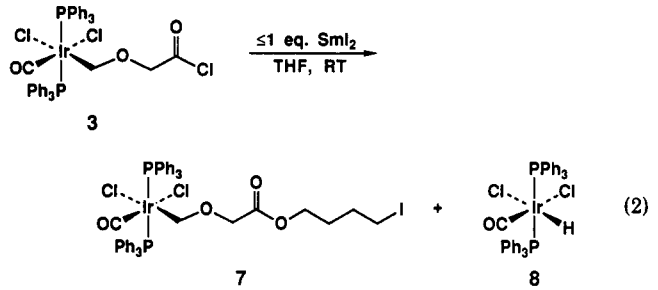
(17) Discharge of the blue color characteristic of samarium(II) is almost immediate (<1 min), indicating that the reductive aspects of this cyclization occur rapidly. The reaction is stirred an additional 12 h at room temperature to allow for complete halide exchange at the metal.[19]



3 6 (1)

an infrared absorption at 1660 cm^{-1} and a characteristic low-field acyl resonance at δ 229.5 in the ^{13}C NMR spectrum.[18] The stereochemical assignment of the metal carbonyl and halide ligands is unconfirmed but is assigned on the basis of the unusually low-energy terminal CO absorption at 2020 cm^{-1} in the infrared spectrum,[5,8] suggesting that the CO ligand is trans to the more donating alkyl substituent rather than the acyl moiety. Essentially complete exchange of the chloride ligand for iodide was indicated by the elemental analysis.[19]

A much lower yield of cyclized material was obtained by slow addition of the SmI_2 solution or by addition of less than two reducing equivalents. Under such conditions, two new products were isolated in variable yields, tentatively identified as the open-chain ester complex **7**,[20] formed by a precedented samarium-assisted insertion of tetrahydrofuran solvent into the acyl chloride bond,[14b] and the iridium hydride complex **8**, identical with that obtained by treating Vaska's complex with HCl (eq 2).[21] Although we



(2)

have been unable to isolate complex **7** in analytically pure form, the structural formulation is strongly supported by spectroscopic analysis, particularly the infrared absorption at 1750 cm^{-1}, and both ^1H and ^{13} NMR spectroscopy,[20] including decoupling experiments. Elemental analysis indicates that partial halide exchange at the iridium center has occurred; however, no further incorporation of iodide is obtained when this material is treated with excess NaI in acetone at room temperature for several days. Spectroscopically identical material can be prepared by independent synthesis: treatment of acid chloride complex **3** with 4-chloro-1-butanol followed by halogen exchange with excess NaI in acetone. Ring opening of THF is not observed in the absence of SmI_2, nor is cyclized acyl **6** formed on treatment of **7** with additional SmI_2.

The dependence of the product distribution on the stoichiometry and relative concentration of SmI_2 is completely analogous to the reactivity observed for organic acid chlorides reported by Kagan,[14b] leading to the perhaps surprising conclusion that the reaction of both equivalents of SmI_2 occurs at the organic acyl functionality and not at the electrophilic metal center. Reduction of the acid chloride is rapid (for organic acid chlorides, <0.5–4 min for complete consumption of 2 equiv of SmI_2[14b]) and, in the presence of two reducing equivalents, leads to a proposed acyl samarium complex ($RCOSmI_2$), which reacts as a nucleophile at the metal center. Also as reported by Kagan, under samarium-deficient conditions, the strongly Lewis acidic Sm(III) formed on partial conversion of the starting acid halide subsequently catalyzes the observed ring opening and insertion of THF into the acid halide. Considerably more speculative is the origin of the iridium(III) hydride complex, which possibly arises from decarbonylation and fragmentation of the acyl radical formed upon one-electron reduction, followed by facile hydrogen abstraction from THF by the resultant metal-centered radical.

Interestingly, SmI_2 does not appear to provide a general solution to intramolecular reductive cyclization of pendant acid chloride complexes. No cyclized material was recovered from the reaction of all-carbon complex **5** with SmI_2 (or Na/Hg), underscoring the delicate balance between reductive cyclization and other reaction pathways in this system. Such generality may require modification of the acid chloride functionality, providing an electronically less activated acyl derivative for selective reduction at the metal–halide bond.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Union Carbide Innovation Recognition Award Program is gratefully acknowledged. We thank J. B. Wakefield for experimental assistance.

(18) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981; pp 147–150.

(19) The extent of halide metathesis, presumably promoted by Sm(III) halide salts, appears to be dependent on reaction time, complicating purification and elemental analysis of complexes resulting from treatment with SmI_2.

(20) Spectroscopic data for complex **7**: IR (KBr) ν_{CO} 2050, 1750 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 1.69 (m, 2 H), 1.83 (m, 2 H), 2.99 (s, 2 H), 3.22 (t, J_{HH} = 6.6 Hz, 2 H), 4.03 (t, J_{HH} = 6.8 Hz, 2 H), 4.65 (t, J_{PH} = 5.2 Hz, 2 H), 7.45 (m, 18 H), 8.07 (m, 12 H); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 6.4, 29.9, 30.3, 60.6 (br, s), 63.5, 70.8, 128.2 (br s), 131.0, 135.2 (br s), ipso carbon not resolved, 160.5 (t, J_{PC} = 6.9 Hz), 170.0. Anal. Calcd for $C_{44}H_{42}Cl_2IO_4P_2Ir$: C, 48.05; H, 3.94. Found: C, 46.42; H, 3.93.

(21) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 5325. Blake, D. M.; Kubota, M. *J. Am. Chem. Soc.* **1970**, *92*, 2578. See also: Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201.