Straightforward Formation of Carbocations from Tertiary Carboxylic Acids via CO Release at Room Temperature

Nicolò Bartalucci, Marco Bortoluzzi, Stefano Zacchini, Guido Pampaloni, and Fabio Marchetti

Abstract. We report an unprecedented mode of reactivity of carboxylic acids. A series of tertiary carboxylic acids, containing at least one phenyl α-substituent, undergo loss of carbon monoxide at room temperature (295 K), by one pot reaction with 0.5-1 molar equivalents of WCl₆ in dichloromethane. A plausible mechanism for the Ph₃C=CCOOH/WCl₆ reaction, leading to [CP₃][WOCl₄] and Ph₂CCl, is proposed on the basis of DFT calculations. The analogous reactions involving CEt₃CO₂H, CMe₃(Ph)₂CO₂H and CMe₂(Ph)CH₂CO₂H selectively afforded stable hydrocarbons (alkene or indene, depending on the case), apparently resulting from the rearrangement of elusive tertiary carbocations.

Carboxylic acids are key functional groups in organic chemistry, being involved in a wide variety of synthetic routes. In a number of useful transformations, the carboxylic acid unit may act as a leaving one, with elimination of either carbon dioxide or, less frequently, carbon monoxide. Concerning the decarboxylation reactions, leading to valuable alkenes. Remarkably, the decarboxylation of a palladium-acetate complex was recently detected upon thermal decomposition in the gas phase by means of a mass spectrometry experiment. Also carboxylic acid chlorides may be susceptible to metal mediated CO release under thermal treatment, proceeding with an oxidative addition mechanism.

Herein, we present the unique chemistry recognized for a series of tertiary carboxylic acids, containing a variable number of phenyl α-substituents, when allowed to interact with a high valent metal chloride at room temperature. Thus, the 1:1 molar reaction of WCl₆ with triphenylacetic acid in dichloromethane afforded [CP₃][WOCl₄], and Ph₂CCl, 1, in ca. 1:2 molar ratio (NMR), see Scheme 1. Abundant formation of carbon monoxide was detected by gas chromatography.

Scheme 1. Reactions of WCl₆ with tertiary α-phenyl carboxylic acids at room temperature.

The salt 1 was isolated in 32% yield after work-up, and then characterized by X-ray diffraction, analytical and spectroscopic methods (see Supporting Information for details). The crystal structure of 1 (Figure 1) consists of an ionic packing of [CP₃]⁺ cations and [WOCl₄]⁻ anions, both displaying the expected bonding parameters.
It is a common feature of coordination chemistry that the addition of carboxylic acids (including triphenylacetic acid) to metal chlorides proceeds with HCl release and affords the corresponding, stable metal-carboxylates. However, the generation of acid chlorides by CI/O interchange may be viable when oxophilic metal species are involved. With reference to tungsten hexachloride, it was previously found that the reactions with a number of aliphatic and aromatic carboxylic acids are non-selective, leading to mixtures of metal carboxylates and acid chlorides.

To the best of our knowledge and to a general extent, the one pot formation of carboxations from tertiary carboxylic acids (through CO elimination) is unprecedented.

Based on the experimental facts, a plausible pathway for the WCl₅/Ph₃CCO₂H reaction was traced by DFT calculations (Scheme 2).

In accordance with this DFT outcome, monitoring the WCl₅/Ph₃CCO₂H reaction by IR and NMR spectroscopy revealed the intermediate formation of Ph₃CC(O)Cl. Accordingly, the reaction of WOCl₅ with Ph₃CC(O)Cl, freshly prepared from Ph₃CCl and PCl₅, finally yielded a mixture of Ph₃CCl and Ph₃CC(O)Cl as stationary point (c), with a strong lowering of the Gibbs free energy.

In summary, we have described for the first time the one pot CO elimination reaction from the carboxylic acid function occurring at room temperature, as favoured by phenyl α-substituent(s) and promoted by stoichiometric amounts of W(VI) hexachloride. Thus, tertiary carboxylic acids undergo conversion into the corresponding acid chlorides, presumably followed by formation of oxocarbonium cations and then carboxations (also Ph₃CCl was obtained from triphenylacetic acid).

The present investigation was extended to a selection of phenylacetic acids, whose reactions with WCl₅ were checked by GC and NMR analyses. Significant amounts of CO were found to be released from CMe₃(Ph)CO₂H, CPh₃(Me)CO₂H, CPh₃(Et)CO₂H, CPh₃(Pr)CO₂H, CPh₃(CH₃CH₂Br)CO₂H, and CPh₃(C₆H₅)₂CO₂H (1-phenyl-1-cyclohexanecarboxylic acid). Organic products could be cleanly isolated in a limited number of cases, and in particular the alkene Ph₃C=CH(Me), 3, was obtained from WCl₅/CPh₃EtCO₂H. The reactions of WCl₅ with CMe₃(Ph)CO₂H and CPh₃(Me)CO₂H were conveniently performed using 1.2 stoichiometry, and afforded the indenes 4a-b over a precipitate of gray WO₂Cl₁₉ (IR, elemental analysis), as the by-product of Scheme 1.

Compounds 3 and 4a-b were efficiently isolated in 62-88% yields after hydrolysis of the respective reaction mixtures and subsequent purification of the organic phase by chromatography on alumina, and then characterized by elemental analysis, IR and NMR spectroscopy. Furthermore, the molecular structure of 4a was elucidated by a single crystal X-ray diffraction study (a view of the structure is supplied in the SI, Figure S34).

Analogously to the formation of 1-2 from WCl₅/Ph₃CCO₂H, the synthesis of 3-4 takes place through the preliminary formation of the carboxylic acid chlorides (detected by NMR). These should reasonably convert into the elusive carboxations [Ph₃C(Me)(R)]⁺ (R = Me, 1-methyl-1-phenylethyllium; Et, 1-diphenyldimethylpropyl; Ph, 1-diphenylethyllium), to finally afford 3-4. Evidence was collected for the formation of [CPh₃(Me)]⁺ along the route to 4a (H NMR resonances at 7.8 and 3.9 ppm, see SI for details). On the other hand, [Ph₃C(Me)(Et)]⁺ was previously found in equilibrium with its deprotonated form 3, while 4b was observed from the degradation of [PhC(Me)₃]⁺ at T > -40 °C. Up to now, carboxations [PhC(Me)(R)]⁺ (R = Me, Et, Ph) have been generated using various strategies, i.e. by protonation of alkenes or alcohols in strongly acidic media, photolysis of alkene, oxygen or dimeric precursors, hydrogen/chloride abstraction from quaternary hydrocarbons, and photochemical N₂ extrusion from indazoles.

In summary, we have described for the first time the one pot CO elimination reaction from the carboxylic acid function occurring at room temperature, as favoured by phenyl α-substituent(s) and promoted by stoichiometric amounts of W(VI) hexachloride. Thus, tertiary carboxylic acids undergo conversion into the corresponding acid chlorides, presumably followed by formation of oxocarbonium cations and then carboxations (also Ph₃CCl was obtained from triphenylacetic acid). The latter are relatively

Figure 1. Molecular structure of [CPh₃][WOCl₅], 1, with key atoms labelled. Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (°): W(1)-(O(1)) 1.650(4), W(1)-(Cl(1)) 2.4898(16), W(1)-(Cl(2)) 2.3711(16), W(1)-(Cl(3)) 2.3401(15), W(1)-(Cl(4)) 2.3154(18), W(1)-(Cl(5)) 2.3280(15), C(1)-(C(2)) 1.445(9), C(1)-(C(8)) 1.449(9), C(1)-(Cl(4)) 1.443(9), O(1)-(W(1)-(Cl(1)) 173.91(17), Cl(3)-(W(3)-(Cl(5)) 172.86(6), Cl(2)-(W(2)-(Cl(4)) 170.21(6), C(2)-(C(1)-(C(14)) 121.6(6), C(8)-(C(1)-(C(14)) 118.8(6), C(2)-(C(1)-(C(8)) 120.0(6).

Scheme 2. DFT-calculated reaction pathway for the conversion of WCl₅ and Ph₃CCO₂H to [CPh₃][WOCl₅] (1), Ph₃CCl, 2, and [WOCl₅]. Relative Gibbs free energies in kcal mol⁻¹, Transition states in red. C-PCM/ωB97X calculations, dichloromethane as continuous medium.
stabilized by the α-phenyl substituents, and evolve to stable hydrocarbons according to their characteristic nature and chemistry. The viability of this unusual reactivity seems related to the multiskilling role played by WCl₆, being a strong Lewis acid, effective chlorinating agent and precursor of the stabilizing WOC₂⁻ counteranion. Errore: sorgente del riferimento non trovata. It is noteworthy that, in contrast, the typical decarboxylation of carboxylic acid chlorides requires high temperatures and intermediate oxidative addition to redox active metal centres.

Acknowledgments
We are grateful to Mr. Francesco Del Cima and Dr. Debora Preti for executing GC analyses, to Ms. Gioia Marrazzini for assistance with the experimental work and to the University of Pisa for financial support (Fondi di Ateneo 2017).

Notes and references

Scheme 2.