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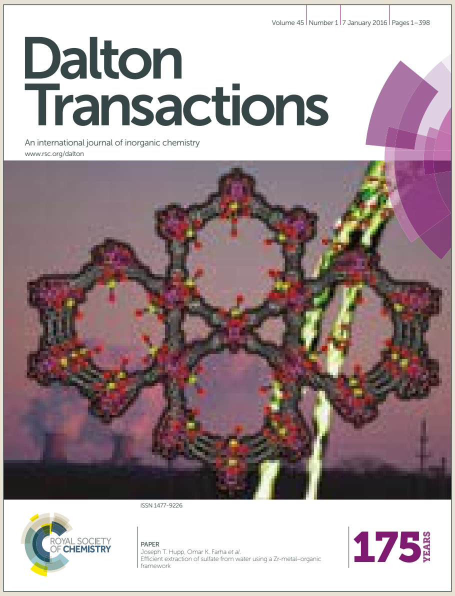

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Decarbonylation of Phenylacetic Acids by High Valent Transition Metal Halides

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Abstract

Triphenylacetic acid underwent unusual decarbonylation when allowed to react with a series of halides of groups 4-6 metals in their highest oxidation state, in dichloromethane at ambient temperature. Thus, the reaction of CPh_3COOH with $MoCl_5$, in 1:1 molar ratio, afforded the trityl salt $[CPh_3][MoOCl_4]$, **1**, in 79% yield, while the 1:2 reaction of CPh_3COOH with NbF_5 afforded $[CPh_3][NbF_6]$, **2**, in 70% yield $NbOF_3$ being the metal co-product. CPh_3COOH reacted with $NbCl_5$, TiF_4 and $WOCl_4$ to give mixtures of compounds, however the cation $[CPh_3]^+$ was NMR identified in each case. $[CPh_3][NbCl_6]$, **3**, was isolated from $NbCl_5$ and CPh_3COCl, prior generated from CPh_3COOH and PCl_5. The reaction of CPh_3COOH with $TiCl_4$ was non-selective, and the salt $[CPh_3][Ti_2Cl_8(\mu\text{-}\kappa^2\text{-}O_2CCPh_3)]$, **4**, was obtained in 18% yield. The decarbonylation reactions of $CMe(Ph)_2COCl$ and $CMe_2(Ph)COCl$ by means of $NbCl_5$ led to the indanes **5a-b**, which were isolated in 79-97% yields after hydrolysis of the mixtures and subsequent alumina filtration of the organic phases. The reactions of $CH(Ph)_2COOH$ with $NbCl_5$ and WCl_6 afforded $NbCl_4(OOCCHPh_2)$, **6**, and $CHPh_2COCl$, respectively, as the prevalent species. $CPh_2(CH_2CH_2Br)COOH$ did not undergo CO release when allowed to interact with WCl_6, instead selective intramolecular condensation to $\overline{\mathrm{C(Ph)_2C(=O)OCH_2C}}\mathrm{H_2}$, **7**, occurred. MeC≡CCOOH underwent hydrochlorination by WCl_6 to give MeC(Cl)=CHCOOH, **8**, in 72% yield. All the products were fully characterized by elemental analysis, IR and multinuclear NMR spectroscopy. In addition, the solid state structures of **1**, **2**, **4**, **7**, **8** were elucidated by X-ray diffraction.

Introduction

Early transition metal halides, containing the metal in an oxidation state higher than +4, are featured by a strong Lewis acidic character[1] and a quite positive oxidation potential.[2] These peculiar characteristics give raise to several transformations on organic substrates, such as the formation of C-C

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bonds,[3] the dehydrogenative coupling of arenes,[4] the functionalization of alkenes,[5] the polymerization of alkynes [6] and several cycloaddition reactions.[7]

In the recent years, we have studied the reactivity of high valent groups 4, 5 and 6 metal halides with Lewis bases pointing out a marked difference of reactivity when moving from group 4 to group 6 elements.

For example, $TiCl_4$ generally reacts with oxygen donors affording hexacoordinate complexes, and activation of the ligands is observed at high temperature only.[8] On the other hand, in view of the lower M-Cl bond energy[9] and the higher oxidation state, $MoCl_5$ and WCl_6 make possible stoichiometric modifications of simple molecules through unconventional pathways even at room temperature or below. In particular, tungsten hexachloride shows examples which include the conversion of imines into aza-2-allenium and nitrilium cations, [10] the former being generated via unusual N_2 elimination, and of α-diimines into quinoxalinium salts.[11]

Unique reactivity patterns have been observed with niobium and tantalum pentahalides[1c,7,12] and, considering also the relative cheapness and the substantial non-toxicity of the related metal elements,[13] a significant advance in the use of these systems as promoters for organic transformations has been experienced in the last years.[7,14] When compared to the heavier halides of Group 6, NbX_5 (X = F, Cl) are more inert towards reduction processes, and are characterized by relatively strong niobium-halide bonds,[9] thus disfavouring halide/oxygen exchange reactions.[15] As a matter of fact, NbF_5 forms adducts when allowed to react with alcohols and carboxylic acids,[16] while $NbCl_5$ in the same conditions affords metal alcoholates/carboxylates through HCl release.[14e, 17] The formation of metal carboxylates is also the typical reactivity displayed by low- or medium valent transition metal chlorides with carboxylic acids,[18] including CPh_3COOH.[19] On the other hand, the reactivity of simple carboxylic acids (RCOOH) with $MoCl_5$ and WCl_6 shows similitudes with the behaviour of PCl_5,[20] thus Cl/O exchange takes place with formation of the corresponding acyl chlorides RC(O)Cl. This outcome, however, is

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often accompanied by side reactions,[21] possibly giving an explanation why the interaction of Group 6 high valent metal halides with carboxylic acids (and their acyl chloride counterparts), especially the ones bearing an additional functional group, has been sparingly explored heretofore.

In the framework of our project, aimed to develop the chemistry of homoleptic halides of early transition metals, and following our recent communication on the unusual reactivity exhibited by WCl_6 with CPh_3COOH and related carboxylic acids,[22] herein we report an extension of this study to other halides of high valent groups 4-6 metals.

Results and discussion

1. Decarbonylation reactions of triphenylacetic acid.

The 1:1 molar reactions of triphenylacetic acid with a series of high valent metal chlorides/fluorides, i.e. $MoCl_5$, $WOCl_4$, $NbCl_5$, NbF_5 or TiF_4, were carried out in dichloromethane at ambient temperature and cleanly proceeded with CO extrusion (detected by gas-chromatography), to give the trityl cation associated to various counteranions (Scheme 1). Similarly to what found for the CPh_3COOH/WCl_6 reaction system,[22] the preliminary formation of CPh_3COX (X = Cl or F), resulting from halide/oxygen exchange between the organic substrate and the metal halide, is likely to precede the CO release step. Indeed, CPh_3COCl was NMR detected along the pathways to **1** and **3**. Olah observed a very unstable coordination complex between CPh_3COF and SbF_5, decarbonylating to $[CPh_3]^+$.[23]

The reaction involving $MoCl_5$ straightforwardly afforded **1**, isolated in 78% yield, wherein the anion is the Cl/O exchange metal product (Scheme 1a). On the other hand, the cation $[CPh_3]^+$ was clearly recognized by ^{13}C NMR in the reaction mixtures obtained from $CPh_3COOH/WOCl_4$ and CPh_3COOH/TiF_4 (diagnostic resonance at ca. 210 ppm), but the clean isolation of products failed (Scheme 1b). The ^{19}F NMR spectrum of CPh_3COOH/TiF_4 displayed a complicated set of signals.

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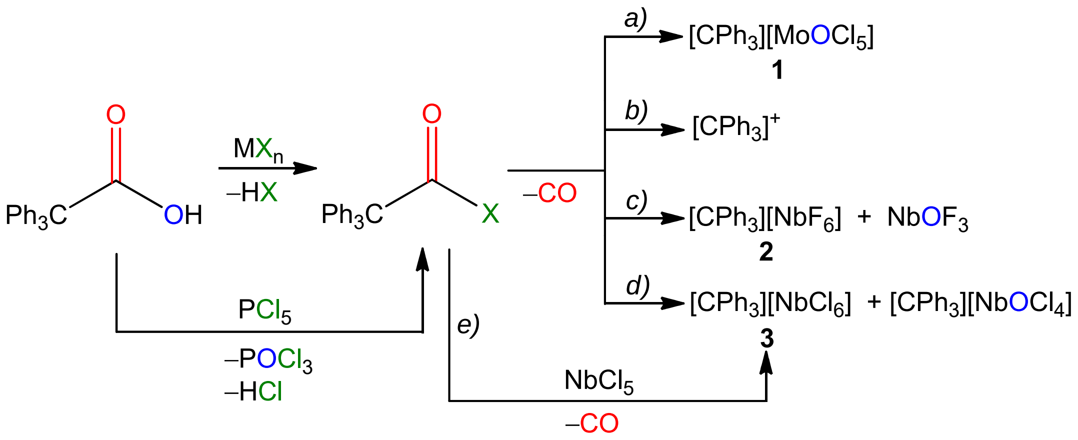

Scheme 1. Decarbonylation of triphenylacetic acid and triphenylacetic acid chloride by reactions with high valent halides. MX_n = $MoCl_5$ (a); $WOCl_4$ or TiF_4 (b); NbF_5 (c); $NbCl_5$ (d).

The combination of CPh_3COOH with niobium pentahalides yielded **2-3** in admixture with niobium oxo-halide co-products (Scheme 1c-d), and the optimal stoichiometry for these reactions resulted to be Nb/acid 2:1 (Eqn. 1). In other terms, it appears that half of the metal reactant serves the halide/O exchange, whereas the remaining aliquot is employed to form the anion within **2-3**. $NbOF_3$ was easily separated by precipitation and characterized by IR spectroscopy (typical band at 995 cm^{-1}),[24] thus allowing the isolation of **2**.

$$2\ NbX_5 + CPh_3COOH \rightarrow [CPh_3][NbX_6] + CO + HX + NbOX_3 \qquad (1)$$

X = F, Cl

Both anions $[NbCl_6]^-$ (δ = 8.8 ppm)[25] and $[NbOCl_4]^-$ (δ = –343 ppm)[26] were identified by ^{93}Nb NMR in the reaction system $CPh_3COOH/NbCl_5$, but the isolation of a well-defined product was not possible in this case. The IR spectrum of the solid residue suggested the presence of $NbOCl_3$ (broad absorption at 780 cm^{-1}).[27]

In order to cleanly generate **3**, CPh_3COCl was prior generated from CPh_3COOH and PCl_5, and then allowed to react with $NbCl_5$ (Scheme 1e).

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Compounds **1-3** were characterized by elemental analysis, IR and multinuclear NMR spectroscopy. Salient data are represented by IR band due to the Mo=O moiety in **1** (ν = 993 cm^{-1})[28] and ^{19}F NMR resonance related to the [NbF$_6$]$^-$ anion in **2** (decet centred at 102 ppm).[29] Furthermore, the solid state structures of **1** and **2** were elucidated by single crystal X-ray diffraction studies. Views of these structures are shown in Figures 1 and 2, while relevant bonding parameters are reported in Tables 1-2.

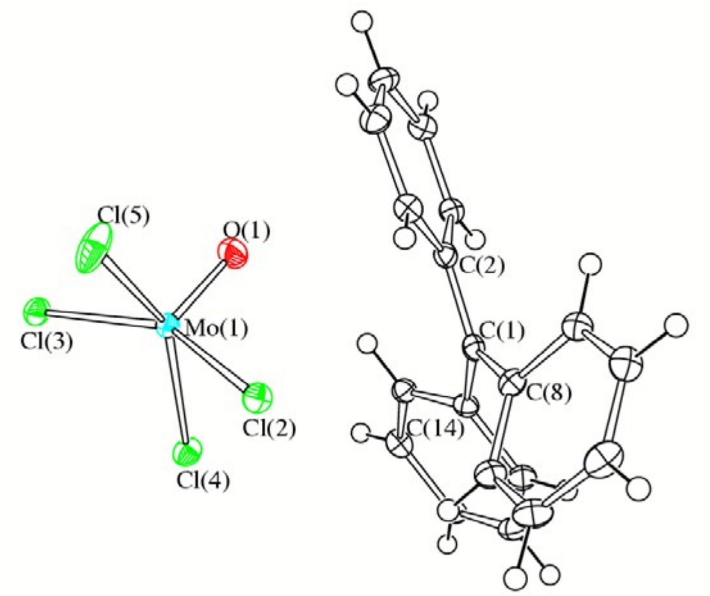

Figure 1. Molecular structure of [CPh$_3$][MoOCl$_4$], **1**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level.

Table 1. Selected bond distances (Å) and angles (°) for **1**.

Mo(1)–O(1)	1.6549(14)	Mo(1)–Cl(2)	2.3527(5)
Mo(1)–Cl(3)	2.3484(5)	Mo(1)–Cl(4)	2.3427(5)
Mo(1)–Cl(5)	2.3320(6)	C(1)–C(2)	1.444(2)
C(1)–C(8)	1.455(2)	C(1)–C(14)	1.442(2)
O(1)–Mo(1)–Cl(2)	105.27(5)	O(1)–Mo(1)–Cl(3)	104.49(5)
O(1)–Mo(1)–Cl(4)	105.66(5)	O(1)–Mo(1)–Cl(5)	105.51(6)
Cl(2)–Mo(1)–Cl(3)	150.226(17)	Cl(4)–Mo(1)–Cl(5)	148.82(2)
C(2)–C(1)–C(8)	119.34(15)	C(2)–C(1)–C(14)	121.35(15)
C(8)–C(1)–C(14)	119.31(15)		

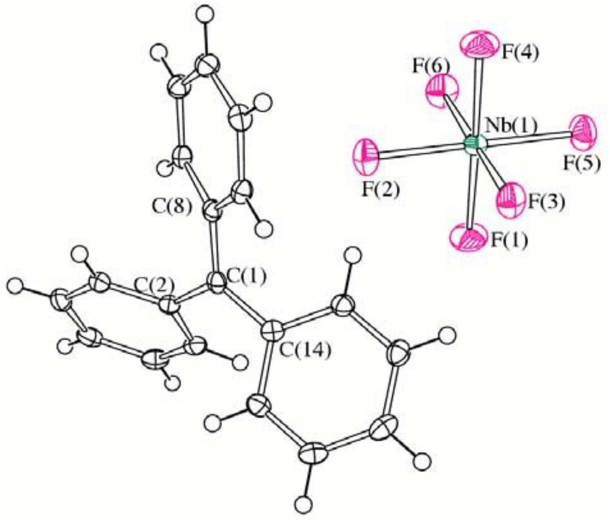

Figure 2. Molecular structure of [CPh_3][NbF_6], **2**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level.

Table 2. Selected bond distances (Å) and angles (°) for **2**.

Nb(1)–F(1)	1.8698(13)	Nb(1)–F(2)	1.8963(13)
Nb(1)–F(3)	1.8885(13)	Nb(1)–F(4)	1.8774(13)
Nb(1)–F(5)	1.8919(14)	Nb(1)–F(6)	1.8892(13)
C(1)–C(2)	1.447(3)	C(1)–C(8)	1.440(3)
C(1)–C(14)	1.452(3)		
F(1)–Nb(1)–F(4)	178.25(6)	F(2)–Nb(1)-F(5)	179.20(5)
F(3)–Nb(1)–F(6)	178.39(6)	C(2)–C(1)–C(8)	120.79(18)
C(2)–C(1)–C(14)	118.87(18)	C(8)–C(1)–C(14)	120.29(18)

The solid state structure of **1** is an ionic packing of [CPh_3]$^+$ cations and [$MoOCl_4$]$^-$ anions. The former cation has been previously characterized with miscellaneous anions showing very similar bonding parameters.[30] The [$MoOCl_4$]$^-$ anion displays a distorted square-pyramidal structure as previously found in other [$MoOCl_4$]$^-$ salts.[17a, 28f, 31] The Mo(1)–O(1) bond [1.6549(14) Å] reveals a strong π-character, as expected for a Mo(V)=O unit.[32] The [$MoOCl_4$]$^-$ anions may be found in the solid state in different forms: (A) isolated anions; (B) weak intermolecular adducts with a donor atom of the cation or the co-crystallized solvent molecule; (C) dimeric $\{[MoOCl_4]^-\}_2$ units; (D) infinite $\{[MoOCl_4]^-\}_\infty$ chains.[31] In the case of **1**, the [$MoOCl_4$]$^-$ anions are isolated (A). The solid state structure of **2** consists of an ionic packing of [CPh_3]$^+$ cations and [NbF_6]$^-$ anions,[15b, 25c, 33] which have been previously described in the literature.

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The study of the reactivity of triphenylacetic acid with metal halides was extended to titanium tetrachloride. The 1:1 molar reaction afforded a complicated mixture of products. Fractional crystallization of the raw material afforded a 18% yield of the crystalline salt [CPh_3][$Ti_2Cl_8(O_2CCPh_3)$], **4**. This outcome indicates that $TiCl_4$ exhibits a hybrid behaviour towards triphenylacetic acid, the latter being partially converted into carboxylate and partially decarbonylated, thus determining the non-selectivity of the reaction. The scarcely soluble compound **4** was characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. The solid state structure of **4** consists of an ionic packing of $[CPh_3]^+$ cations and $[Ti_2Cl_8(OOCCPh_3)]^-$ anions. The latter anion is unprecedented and closely related to the previously reported neutral species $Ti_2Cl_7(O_2CR)(RCOOH)$ (R = p-C_6H_4Cl, CH=CHMe),[34] wherein a terminal chloride ligand has been replaced by a O-bonded CPh_3COO fragment. Thus, $[Ti_2Cl_8(OOCCPh_3)]^-$ is a dimeric anion, composed by two distorted octahedral Ti(IV) centres, each bonded to three terminal and two μ-bridging chlorides as well as the O-atom of a bridging $[Ph_3CCOO]^-$ carboxylate ligand. All bonding parameters closely resemble those reported in the case of $Ti_2Cl_7(O_2CR)(RCOOH)$.[34] The carboxylate ligand gives rise to a strong IR absorption at 1644 cm^{-1}, to be compared with the value 1693 cm^{-1}, characteristic of CPh_3COOH.

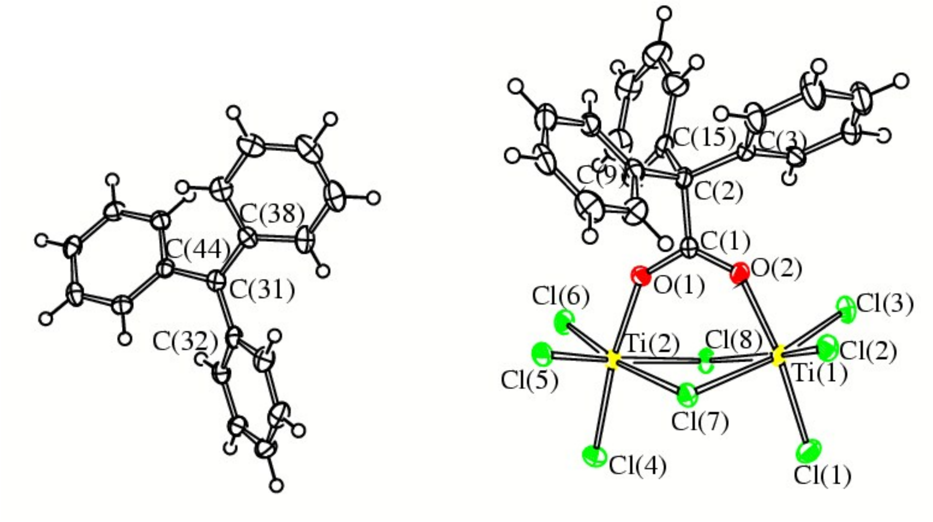

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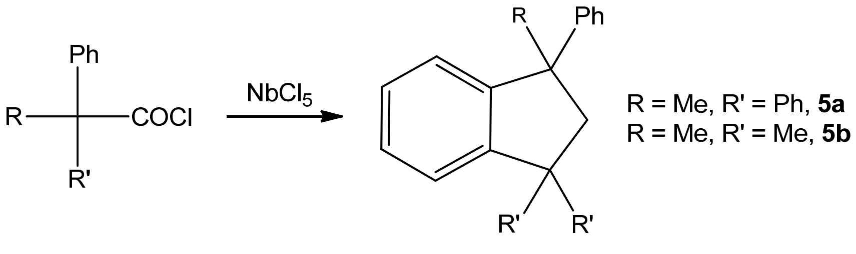
Figure 3. Molecular structure of $[CPh_3][Ti_2Cl_8(OOCCPh_3)]$, **4**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level.

Table 3. Selected bond distances (Å) and angles (°) for **4**.

Ti(1)–O(2)	2.008(4)	Ti(2)–O(1)	2.000(3)
Ti(1)–Cl(1)	2.2406(16)	Ti(2)–Cl(4)	2.2402(16)
Ti(1)–Cl(2)	2.2165(16)	Ti(2)–Cl(5)	2.2205(16)
Ti(1)–Cl(3)	2.2368(16)	Ti(2)–Cl(6)	2.2272(16)
Ti(1)–Cl(7)	2.4790(15)	Ti(2)–Cl(7)	2.4835(15)
Ti(1)–Cl(8)	2.5054(15)	Ti(2)–Cl(8)	2.5051(15)
C(1)–O(1)	1.262(6)	C(1)–O(2)	1.249(6)
C(1)–C(2)	1.534(7)	C(2)–C(3)	1.550(7)
C(2)–C(9)	1.536(7)	C(2)–C(15)	1.560(7)
C(31)–C(32)	1.447(7)	C(31)–C(38)	1.433(7)
C(31)–C(44)	1.454(7)		
O(2)–Ti(1)–Cl(1)	170.42(11)	O(1)–Ti(2)–Cl(4)	171.96(11)
Cl(2)–Ti(1)–Cl(8)	166.45(6)	Cl(5)–Ti(2)–Cl(8))	165.76(6)
Cl(3)–Ti(1)–Cl(7)	168.12(6)	Cl(6)–Ti(2)–Cl(7)	168.41(6)
Cl(2)–Ti(1)–Cl(3))	99.84(6)	Cl(5)–Ti(2)–Cl(6)	101.52(6)
Cl(7)–Ti(1)–Cl(8)	79.15(5)	Cl(7)–Ti(2)–Cl(8)	79.07(5)
Ti(1)–Cl(7)–Ti(2)	97.73(5)	Ti(1)–Cl(8)–Ti(2)	96.48(5)
Ti(1)–O(2)–C(1)	141.4(3)	Ti(2)–O(1)–C(1)	140.1(3)
O(1)–C(1)–O(2)	123.2(5)	O(1)–C(1)–C(2)	116.7(4)
O(2)–C(1)–C(2)	120.1(4)	C(1)–C(2)–C(3)	109.8(4)
C(1)–C(2)–C(9)	105.4(4)	C(1)–C(2)–C(15)	110.3(4)
C(32)–C(31)–C(38)	119.8(5)	C(32)–C(31)–C(44)	118.7(5)
C(38)–C(31)–C(44)	119.8(5)		

2. Decarbonylation reactions and activation reactions of mono- and diphenylacetic acids.

The reactions of $CMePh_2COCl$ and $CMe_2PhCOCl$ with $NbCl_5$ proceed as reported in Scheme 2 affording the indanes **5a-b**, which were isolated in good yields **(**after hydrolysis of the mixtures and subsequent alumina filtration of the organic phases) and characterized analytically and spectroscopically. Compound **5b** was also obtained, although in a lower yield, by using $NbOCl_3$ in the place of $NbCl_5$.



Scheme 2. Synthesis of indanes by reaction of phenylacetic acids with $NbCl_5$.

Indanes were previously obtained by elaborated protocols consisting in dimerization of cyclobutenes constructed by coupling of C_2 blocks.[35]

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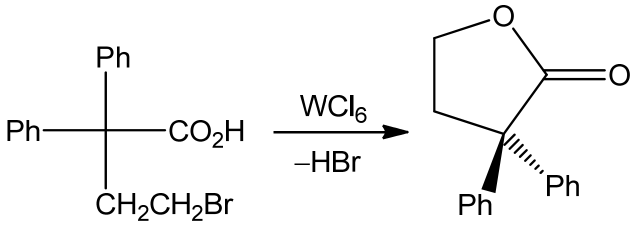
The reactivity of diphenylacetic acid was investigated towards $NbCl_5$ and WCl_6. Both reactions failed to produce decarbonylation products, and instead evidenced the typical reactivity of the two chlorides towards carboxylic acids.[17b, c, 21a, 36] Thus, $NbCl_4(O_2CCHPh_2)$, **6**, was isolated in good yield and fully characterized (Eqn. 2), while $CHPh_2COCl$ was the only species NMR detected in the WCl_6/acid reaction solution (Eqn. 3).

$$NbCl_5 + CHPh_2COOH \rightarrow \underset{\mathbf{6}}{NbCl_4(O_2CCHPh_2)} \qquad (2)$$

$$WCl_6 + CHPh_2COOH \rightarrow CHPh_2COCl + WOCl_4 \qquad (3)$$

It is presumable that the relative instability of the carbocation $[CHPh_2]^+$ [37] is responsible for not observing decarbonylation from diphenylacetic acid.[22]

The interaction of 4-bromo-2,2-diphenylbutyric acid with WCl_6 led to cyclization of the organic substrate via HBr release, affording **7** in high yield. In this case, the presence of bromine as a β-substituent is the key for inhibiting the decarbonylation pathway.



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The product **7** was purified by alumina chromatography and characterized by analytical and spectroscopic techniques, and its identity confirmed by X-ray diffraction (Figure S1 and Table S1). The ester group manifests itself with a strong IR absorption at 1762 cm^{-1} and a ^{13}C NMR resonance at 177.8 ppm.

Finally, the reaction of WCl_6 with an alkynyl carboxylic acid, i.e. MeC≡CCOOH, was investigated in dichloromethane. This reaction resulted in the prevalent hydrochlorination of the triple carbon-carbon

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bond, affording MeC(Cl)=CHCOOH, **8**, which was identified by IR and NMR spectroscopy and X-ray diffraction (Figure S2 and Table S2).

Conclusions

The carboxylic acid function, in organic chemistry, can act as a leaving one, with elimination of either carbon dioxide or, less frequently, carbon monoxide. The decarbonylation reactions, leading to alkenes or C−C coupling products, are usually promoted by low valent transition metal compounds and take place under harsh conditions (typically, temperatures above 150 °C).[22]

We have previously found that the decarbonylation pathway is straightforward for α-phenylacetic acids at room temperature in the presence of WCl_6, through the preliminary formation of the related carboxylic acid chlorides. Herein, we have demonstrated that this non-conventional mode of reactivity has some general character, thus working with a series of homoleptic halides of high valent transition metals belonging to groups 4-6. However, a minimum oxidation state of +5 for the metal centre seems necessary to make the reaction selective. It should be remarked that triphenylacetic acid typical reacts with low- or medium valent transition metal chlorides affording metal triphenyl-acetates via HCl elimination.[19] Our results indicate that the α-carbon in the carboxylic acid must be fully substituted in order to permit the CO release and the relative stabilization of the descending radical cation, and that the substitution at the β-carbon may also play an important role. The radical cations may then be converted *in situ* into indanes depending on the specific stability/chemistry of the former.

This paper confirms the potential of high valent transition metal halides as promoters of valuable organic transformations, in view of their possible dual role as halogenating agents and oxidants.

Experimental Section.

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Methods and materials. *Warning*: all the metal products reported in this paper are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction and crystallization procedures. The reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. $MoCl_5$ (99.6% purity), $NbCl_5$ (99+%), NbF_5 (99.5%) and TiF_4 (98%) were purchased from Strem and stored in sealed tubes under argon atmosphere. $TiCl_4$ (99.0+%) and carboxylic acids (>97%) were purchased from Sigma-Aldrich or TCI Europe and stored under argon atmosphere as received. $WOCl_4$[38] and $NbOCl_3$[27] were prepared according to the literature. Once isolated, the metal products were conserved in sealed glass tubes under nitrogen. Solvents (Sigma-Aldrich) were distilled before use from appropriate drying agents. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR spectra were recorded at 293 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ^{1}H and ^{13}C were referenced to the non-deuterated aliquot of the solvent; the chemical shifts for ^{19}F and ^{93}Nb were referenced, respectively, to $CFCl_3$ and $[NEt_4][NbCl_6]$ as external references. Gas-chromatographic analyses were carried out on a Dani 3200 instrument, equipped with capillary column with molecular sieves (2m; 0.25in ID), using Ar at $p = 1.5$ atm as a gas carrier, at 50 °C. Carbon and hydrogen analyses were performed on a Vario MICRO cube instrument (Elementar). The chloride content was determined by the Mohr method[39] on solutions prepared by dissolution of the solids in aqueous KOH at boiling temperature, followed by cooling down to ambient temperature and addition of HNO_3 up to neutralization. Titanium content was determined spectrophotometrically by measuring the 410 nm absorbance of an aqueous solution after treatment with few drops of 30% aqueous H_2O_2 (UV-VIS spectrum was recorded with Perkin-Elmer Lambda EZ201 spectrophotometer at 293 K).

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Reaction of $MoCl_5$ with triphenylacetic acid: synthesis of $[CPh_3][MoOCl_4]$, 1. A suspension of $MoCl_5$ (0.250 g, 0.915 mmol) in CH_2Cl_2 (15 mL) was treated with CPh_3COOH (0.270 g, 0.936 mmol). The mixture was stirred at ambient temperature for 18 hours, then the final brown solution was concentrated to *ca.* 3 mL and added of hexane (30 mL). The resulting precipitate was washed with pentane (20 mL) and dried under vacuum: compound **1** was isolated as a dark-red powder. Yield 0.359 g, 79%. Anal. Calcd for $C_{19}H_{15}Cl_4MoO$: C, 45.91; H, 3.04; Cl, 28.53. Found: C, 46.06; H, 3.02; Cl, 28.31. IR (solid state): ν/cm^{-1} = 3062vw, 1579vs, 1479m, 1446s, 1385w, 1352vs, 1292s, 1180m, 1169m, 1098w, 1029w, 993vs (Mo=O), 976w, 949w, 913w, 841w-m, 803m, 768m-sh, 762m, 697vs, 684s. ^1H NMR (CD_2Cl_2): δ/ppm = 8.5, 8.1 (br, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ/ppm = 211.6 (*C*Ph$_3$), 148.3, 147.5, 141.3, 135.1 (Ph). Crystals of **1** suitable for X-ray analysis were collected from a dichloromethane reaction solution layered with hexane and settled aside at −30°C for one week.

Reaction of NbF_5 with triphenylacetic acid: synthesis of $[CPh_3][NbF_6]$, 2, and $NbOF_3$. The reaction of NbF_5 (0.200 g, 1.06 mmol) with CPh_3COOH (0.154 g, 0.534 mmol) was carried out with a procedure analogous to that described for $MoCl_5$/CPh_3COOH. The final yellow solution was separated from a pale-yellow precipitate by filtration. IR analysis on the precipitate clearly evidenced the presence of a strong band at 995 cm^{-1} ($\nu_{Nb=O}$, $NbOF_3$). Compound **2** was recovered from the solution as a yellow solid after work-up. Yield 0.167 g, 70%. Crystals of **2** suitable for X-ray analysis were collected from a dichloromethane reaction solution layered with hexane and stored at −30°C for one week. Anal. Calcd for $C_{19}H_{15}F_6Nb$: C, 50.69; H, 3.36; Nb, 20.64. Found: C, 50.64; H, 3.41; Nb, 20.43. IR (solid state): ν/cm^{-1} = 2958w, 2925w, 1581vs, 1483m, 1449s, 1355vs, 1294s, 1186m, 1169w-m, 1030w, 995w-m, 982w-br, 914w, 846m, 837m, 806m, 765m, 733w, 699vs. ^1H NMR (CD_3CN): δ/ppm = 8.30, 7.88, 7.76 (m, CPh$_3$). $^{13}C\{^1H\}$ NMR (CD_3CN): δ/ppm = 212.0 (*C*Ph$_3$), 143.1, 140.2, 130.1 (Ph). ^{19}F NMR

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(CD_3CN): δ/ppm = 102 (decet, $^1J_{NbF} = 3.4 \cdot 10^2$ Hz, NbF_6^-). ^{93}Nb NMR (CD_3CN): δ/ppm = −1556 (hept, $^1J_{NbF} = 3.4 \cdot 10^2$ Hz, NbF_6^-).

Reaction of $NbCl_5$ with triphenylacetic acid: identification of $[CPh_3]^+$, $[NbCl_6]^-$, $[NbOCl_4]^-$ and $NbOCl_3$. The reaction of $NbCl_5$ (0.110 g, 0.407 mmol) with CPh_3COOH (0.125 g, 0.433 mmol) was carried out with in CD_2Cl_2 (5 mL). The reaction solution was analyzed by NMR spectroscopy after 72 hours. ^{1}H NMR (CD_2Cl_2): δ/ppm = 8.31 (t, $^3J_{HH}$ = 7.4 Hz, 3 H, $[CPh_3]^+_{para}$); 7.94 (t, $^3J_{HH}$ = 7.6 Hz, 6 H, $[CPh_3]^+_{meta}$); 7.73 (d, J = 7.5 Hz, 6 H, $[CPh_3]^+_{ortho}$); 7.32-7.27 (m, CPh_3Cl). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ/ppm = 210.7 (*C*Ph$_3$), 143.5, 142.8, 140.0, 130.7 (Ph). ^{93}Nb NMR (CD_2Cl_2): δ/ppm = 6.6 (Δν½ = 138 Hz, $NbCl_6^-$); −107.2 (Δν½ = 142 Hz, minor); −358 (Δν½ = $2 \cdot 10^3$ Hz, $NbOCl_4^-$); −588 (Δν½ = $6 \cdot 10^4$ Hz, minor). Ratio $NbCl_6^-/NbOCl_4^- \cong 2 : 5$. The IR spectrum of the solid residue obtained by elimination of volatile materials appeared as follows. IR (solid state): ν/cm^{-1} = 3059vw, 1579vs, 1481s, 1447m-s, 1353vs, 1293s, 1183m, 1165w, 1083w, 994m, 835m-sh, 804m, 780br ($\nu_{Nb=O}$, $NbOCl_3$), 763s, 696vs.

Reaction of $NbCl_5$ with triphenylacetic acid chloride: synthesis of $[CPh_3][NbCl_6]$, 3. A solution of CPh_3COOH (172 mg, 0.60 mmol) in CD_2Cl_2 (5 mL) was treated with PCl_5 (123 mg, 0.59 mmol). The mixture was left stirred at ambient temperature for 3 hours. Then $NbCl_5$ (155 mg, 0.57 mmol) was added, and the resulting mixture was stirred at ambient temperature for 48 hours. The volatiles were removed under vacuum, the residue was repeatedly washed with hexane (3 x 20 mL) and then dried under vacuum. Anal. Calcd for $C_{19}H_{15}Cl_6Nb$: C, 41.57; H, 2.75; Cl, 38.75. Found: C, 41.03; H, 2.88; Cl, 38.66. ^{1}H NMR (CD_2Cl_2): δ/ppm = 8.27, 7.90, 7.71 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ/ppm = 211.5 (*C*Ph$_3$), 143.6, 140.8, 131.4, 128.5 (Ph). ^{93}Nb NMR (CD_2Cl_2): δ/ppm = 7.0 ($NbCl_6^-$).

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Reactions of $WOCl_4$/TiF_4 with triphenylacetic acid: identification of $[CPh_3]^+$. The reactions of TiF_4 or $WOCl_4$ (ca. 1 mmol) with 0.5 eq. of CPh_3COOH was carried out with a procedure analogous to that described for $MoCl_5$/CPh_3COOH. The final mixture was eliminated of the volatile materials, then the resulting residue was dried under vacuum.

From TiF_4. IR (yellow solid): ν/cm^{-1} = 3061vw, 1581s, 1485m, 1446m, 1357s, 1295w, 1187w, 866m, 796vs, 758s, 731s, 694vs. ^{1}H NMR (CD_3CN): δ/ppm = 8.30, 7.89, 7.72 (m, CPh_3).

From $WOCl_4$. IR (orange solid): ν/cm^{-1} = 3060vw, 1579vs, 1481s, 1447m-s, 1353vs, 1293s, 1183m, 1165w-m, 1083w, 974m, 832m, 804m, 760s, 696vs. ^{1}H NMR (CD_2Cl_2): δ/ppm = 8.20, 7.89, 7.67 ppm (m, CPh_3). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ/ppm = 210.2 (*C*Ph$_3$), 143.4, 142.9, 140.1, 130.9 (Ph).

Reaction of $TiCl_4$ with triphenylacetic acid: isolation of $[CPh_3][Ti_2Cl_8(\mu\text{-}\kappa^2\text{-}O_2CCPh_3)]$, 4. The reaction of CPh_3COOH (0.280 g, 0.971 mmol) with $TiCl_4$ (1.0 M solution in heptane, 0.97 mL) was carried out with a procedure analogous to that described for $MoCl_5$/CPh_3COOH. IR and NMR analyses on the obtained orange solid residue suggested the formation of a complicated mixture of products. Yellow crystals of **3** suitable for X-ray analysis were isolated from a CH_2Cl_2 reaction mixture layered with hexane and settled aside at −30 °C for 72 h. Yield 0.080 g, 18%. Anal. Calcd for $C_{39}H_{30}Cl_8O_2Ti_2$: C, 51.47; H, 3.32; Cl, 31.17; Ti, 10.52. Found: C, 51.35; H, 3.28; Cl, 31.05; Ti, 10.64. IR (solid state): ν/cm^{-1} = 3059w, 3023w, 1644s(ν_{COO}), 1580w, 1537s, 1493s, 1446m, 1365s, 1334m, 1264w, 1191w, 1160w, 1085w, 1034w, 1002w, 986w, 940w, 904w, 753s-sh, 740vs, 697vs, 669s, 658.

Reaction of $NbCl_5$ with 2,2-diphenylpropionic acid chloride: synthesis of 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene, 5a, (Chart 1).[22,40]

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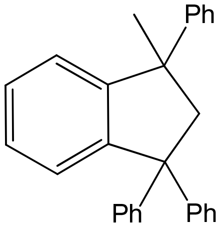

Chart 1. Structure of **5a**.

A solution of $CMePh_2COOH$ (229 mg, 1.01 mmol) in dichloromethane (10 mL) was treated with PCl_5 (209 mg, 1.00 mmol), and the resulting mixture was left stirring at ambient temperature for 2 hours. Then $NbCl_5$ (91 mg, 0.34 mmol) was added, and the mixture was stirred for additional 48 hours. An excess of H_2O (ca. 5 mmol) was added to the final solution, and the so obtained mixture was stirred for 12 hours. Afterwards the organic phase was separated and filtered through an alumina column using diethyl ether as eluent. The product was isolated as a colourless solid upon removal of the volatiles under vacuum. Yield 176 mg, 97%. ^1H NMR (CD_2Cl_2): δ/ppm = 7.49-7.14 (19 H, arom CH); 3.60, 3.28 (d, $^2J_{HH}$ = 13.52 Hz, 2 H, CH_2); 1.71 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ/ppm = 150.6, 149.4, 148.9, 148.6, 147.5 (arom + *C*Ph_2); 128.8, 128.7, 128.0, 127.9, 127.6, 127.4, 126.9, 126.0, 125.7, 125.6, 125.1 (arom); 61.4 (CH_2); 51.2 (Me).

Reaction of niobium chlorides with 2-methyl-2-phenylpropanoic acid chloride: synthesis of 1,1,3-trimethyl-3-phenyl-2,3-dihydro-1H-indene, 5b, (Chart 2).[22,41]

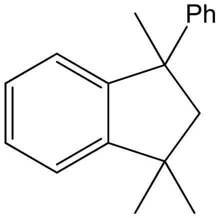

Chart 2. Structure of **5b**.

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A solution of $CMe_2PhCOOH$ (154 mg, 0.94 mmol) in dichloromethane (10 mL) was treated with PCl_5 (200 mg, 0.96 mmol). The resulting solution was left stirring at ambient temperature for ca. 2 hours. Then $NbCl_5$ (85 mg, 0.31 mmol) was added, and the mixture was stirred for additional 48 hours. An excess of H_2O (ca. 5 mmol) was added to the final solution, and the so obtained mixture was stirred for 12 hours. Afterwards the organic phase was separated and filtered through an alumina column using diethyl ether as eluent. The product was isolated as a colourless solid upon removal of the volatiles under vacuum and characterized by elemental analysis and ^{1}H NMR. Yield 88 mg, 79%.

In a different experiment, a dichloromethane solution of freshly prepared 2-methyl-2-phenylpropanoyl chloride was added of 1 eq. of $NbOCl_3$, and the mixture was left stirring at ambient temperature for 5 days. Treatment with water and successive work-up were performed as described above. In this case. the title product was isolated in 70% yield.

Reactions of $CHPh_2COOH$ with metal chlorides.

A) Synthesis of $NbCl_4(O_2CCHPh_2)$, 6. A solution of $CH(Ph)_2COOH$ (230 mg, 1.08 mmol) in CH_2Cl_2 (10 mL) was added of $NbCl_5$ (292 mg, 1.08 mmol). The mixture was stirred at room temperature for 18 hours. The resulting red solution was eliminated of the volatiles, then the residue was washed with hexane (2 x 10 mL) and dried under vacuum. A red solid was obtained. Yield 338 mg, 70%. Anal. Calcd for $C_{14}H_{11}Cl_4NbO_2$: C, 37.71; H, 2.49; Cl, 31.80. Found: C, 37.25; H, 2.50; Cl, 31.70. IR (solid state): ν/cm^{-1} = 3060w, 3027w, 1579s, 1481m, 1447m, 1416m, 1354s, 1295m, 1261w-m, 1180m, 1079w, 1000w, 995w, 978w, 920w, 800vs-br, 733vs, 694vs. ^{1}H NMR (CD_2Cl_2): δ/ppm = 7.44-7.12 (10 H, Ph); 5.37 (s, 1 H, CH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ/ppm = 167.2 (OCO); 143.5-126.1 (Ph); 59.1 (CH). ^{93}Nb NMR ($CDCl_3$): δ/ppm = –234 ($\Delta\nu½ = 2.7\cdot10^3$ Hz).

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B) Formation of CHPh$_2$COCl. A solution of CH(Ph)$_2$COOH (269 mg, 1.27 mmol) in CD$_2$Cl$_2$ (2 mL) was added of WCl$_6$ (251 mg, 0.633 mmol). A light red solution formed after 18 hours, which was analyzed by NMR spectroscopy. The analysis clearly evidenced the formation of CH(Ph)$_2$C(O)Cl,[42] in admixture with a secondary, non-identified species [^{1}H: δ/ppm = 7.50-7.38 (Ph), 5.40 (CH); ^{13}C{^{1}H}: δ/ppm 182.3 (C=O), 136.4 (*ipso*-Ph), 129.1, 128.8, 128.2 (Ph), 57.2 (CH)]. The solution was dried under vacuum, then the residue was characterized by IR spectroscopy. IR (solid state): ν/cm^{-1} = 1702s, 1659s, 1599s, 1581s.

Reactions of WCl$_6$ with 4-bromo-2,2-diphenylbutyric acid: synthesis of 3,3-diphenyldihydrofuran-2(3H)-one, 7, (Chart 3).[43]

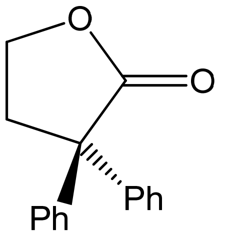

Chart 3. Structure of **7**.

The title compound was obtained by a procedure similar to that described for **5a**, from WCl$_6$ (188 mg, 0.474 mmol) and CPh$_2$(CH$_2$CH$_2$Br)COOH (303 mg, 0.949 mmol), reaction time: 26 h. The product was isolated as colourless crystals upon crystallization from a diethyl ether/pentane mixture, at −30 °C. Yield 197 mg, 72%. Anal. Calcd for C$_{16}$H$_{14}$O$_2$: C, 80.65; H, 5.92. Found: C, 79.75; H, 5.80. IR (solid state): ν/cm^{-1} = 3056w, 2988w, 2912w, 1762vs (C=O), 1596w, 1493m, 1446m, 1369m, 1340w, 1322w, 1226w, 1207w, 1160s, 1090w-m, 1021s, 1000w-m, 954m, 916w, 897w, 834w, 772m, 753s, 725w, 698vs, 675m. ^{1}H NMR (CDCl$_3$): δ/ppm = 7.44-7.29 (10 H, Ph); 4.25 (t, 2 H, J = 6.36 Hz, Ph$_2$CC*H*$_2$); 2.98 (t, 2 H, J = 6.36, 6.85 Hz, CH$_2$Br). ^{13}C{^{1}H} NMR (CDCl$_3$): δ/ppm = 177.8 (C=O); 140.8 (*ipso*-Ph); 128.8, 127.7, 127.6 (Ph); 65.3 (Ph$_2$C*C*H$_2$); 56.5 (*C*Ph$_2$); 37.5 (CH$_2$Br).

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Reaction of MeC≡CCOOH with WCl_6: synthesis of MeC(Cl)=CHCOOH, 8. MeC≡CCOOH (85 mg, 1.01 mmol) and WCl_6 (415 mg, 1.05 mmol) were allowed to react in dichloromethane (30 mL) at room temperature for 7 days. During this period, the progress of the reaction was evaluated by NMR analysis performed on aliquots of the reaction mixture. The final dark red/brown solution was treated with water. The organic phase was then recovered by filtration, and after removal of the volatiles, **8** was recovered as a dark brown solid. Yield 88 mg, 72%. Anal. Calcd. for $C_4H_5ClO_2$: C, 39.86; H, 4.18; Cl, 29.41; O, 26.55. Found: C, 39.71; H, 4.23; Cl, 29.11; O, 26.38. ^{1}H NMR ($CDCl_3$): δ/ppm = 9.2 (br); 6.14, 6.09 (s, 1H, CH *cis* + *trans*); 2.62, 2.33 (s, 3 H, Me *cis* + *trans*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 170.0, 169.2 (C=O *cis* + *trans*); 155.79, 149.50 (=CCl *cis* + *trans*); 118.74, 116.35 (=CH *cis* + *trans*); 28.73, 24.17 (Me *cis* + *trans*).

X-ray quality crystals of **8** were collected from a concentrated solution of the crude product in hexane, stored at −30°C.

Gas chromatographic analyses.

A mixture of metal compound (ca. 1 mmol) and the appropriate carboxylic acid (1 eq.) in CH_2Cl_2 (10 mL) was stirred at ambient temperature for 72 hours in a Schlenk tube tapped with a silicon stopper. An aliquot of the reaction atmosphere was withdrawn by a 1 mL syringe through the stopper and injected into the GC instrument. The yields of CO formation were estimated based on analyses of gaseous standard mixtures containing known amounts of CO. From $MoCl_5/CPh_3COOH$: 45%; from NbF_5/CPh_3COOH: 38%; from $NbCl_5/CPh_3COOH$: 39%; from TiF_4/CPh_3COOH: 9.4%; $WCl_6/CPh_2(CH_2CH_2Br)COOH$: 3.1%; from $WCl_6/CHPh_2COOH$: 0%.

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X-ray Crystallographic studies. Crystal data and collection details for **1**, **2**, **4**·$2CH_2Cl_2$, **6**, **8**, **A1** and **A2** are reported in Table 4. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector (**1**, **2**, **4**·$2CH_2Cl_2$) or a PHOTON100 detector (**6**, **8**, **A1**, **A2**) using *Mo-Kα* radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[44] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[45] Hydrogen atoms were fixed at calculated positions and refined by a riding model. One CH_2Cl_2 molecule of **4**·$2CH_2Cl_2$ is disordered and, thus, it has been split into two positions and refined isotropically using one occupancy factor per disordered group. The CH_2Cl_2 molecules of **4**·$2CH_2Cl_2$ have been restrained to have similar geometries (SAME line in SHELXL; s.u. 0.02) and their C−Cl distances have been restrained to 1.75 Å (s.u. 0.02).

Table 4. Crystal data and experimental details for $[CPh_3][MoOCl_4]$, **1**, $[CPh_3][NbF_6]$, **2**, $[CPh_3][Ti_2Cl_8(\mu-\kappa^2-O_2CCPh_3)]$, **4**·$2CH_2Cl_2$, $\overline{C(Ph)_2C(=O)OCH_2CH_2}$, **6**, MeC(Cl)=CHCOOH, **8**, $CPh_2(CH_2CH_2Br)COOH$, **A1** and $CPh_2(CH_2CH_3)COOH$, **A2**.

	1	**2**	**4**·$2CH_2Cl_2$	**6**	**A1**	**A2**	**8**
Formula	$C_{19}H_{15}Cl_4MoO$	$C_{19}H_{15}F_6Nb$	$C_{41}H_{34}Cl_{12}O_2Ti_2$	$C_{16}H_{14}O_2$	$C_{16}H_{15}BrO_2$	$C_{16}H_{16}O_2$	$C_4H_5ClO_2$
Fw	497.05	450.22	1079.88	238.27	319.19	240.29	120.53
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature, *K*	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	292(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	Pc	Pccn	$P2_1/n$	$P2_1/n$
a, Å	8.9934(15)	8.5095(15)	17.897(3)	7.3476(6)	14.500(3)	9.062(9)	5.387(15)
b, Å	19.335(3)	12.681(2)	10.5524(18)	15.2022(11)	26.776(6)	14.647(14)	9.02(3)
c, Å	11.3379(19)	16.036(3)	25.825(5)	10.9707(9)	7.1309(15)	9.918(10)	11.16(3)
β, □	98.547(2)	94.183(2)	106.889(2)	91.960(3)	90	96.13(2)	101.87(5)
Cell volume, Å^3	1949.6(6)	1725.9(5)	4666.8(14)	1224.71(17)	2768.6(10)	1309(2)	531(3)
Z	4	4	4	4	8	4	4
D_c, g cm^{-3}	1.693	1.733	1.537	1.292	1.532	1.219	1.509
μ, mm^{-1}	1.225	0.757	1.064	0.084	2.964	0.079	0.597
F(000)	988	896	2176	504	1296	512	248
θ limits, °	2.100 - 26.996	2.050 - 27.000	1.234 - 25.026	1.339 - 25.998	1.597 - 24.997	2.490 - 27.990	2.929 - 24.999
Reflections collected	21352	18372	43028	14249	17881	14653	3721
Independent reflections	4254 [R_{int} = 0.0254]	3763 [R_{int} = 0.0335]	8248 [R_{int} = 0.0717]	4780 [R_{int} = 0.0446]	2442 [R_{int} = 0.0841]	3146 [R_{int} = 0.0291]	925 [R_{int} = 0.2230]
Data / restraints / parameters	4254 / 0 /226	3763 / 0 / 235	8248 / 27 / 512	4780 / 2 / 325	2442 / 24 / 173	3146 / 0 / 165	925 / 0 / 66
Goodness on fit on F^2	1.104	1.044	1.045	1.070	1.247	1.081	1.081
$R1$ ($I > 2\sigma(I)$)	0.0227	0.0266	0.0617	0.0489	0.0590	0.0458	0.1338
$wR2$ (all data)	0.0560	0.0647	0.1896	0.0995	0.1285	0.1114	0.3275
Largest diff. peak and hole, e.Å^{-3}	0.528 / -0.587	0.365 / -0.458	2.805 / -1.361	0.192 / -0.272	0.867 / -0.805	0.382 / -0.233	0.550 / -0.511

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Supporting Information. Spectroscopic data of carboxylic acids, figures of the IR and NMR spectra of products. X-ray structures of **6**, **8**, **A1** and **A2**. CCDC reference numbers 1891866 (**1**), 1891867 (**2**), 1891868 (**4**·$2CH_2Cl_2$), 1891869 (**6**), 1891870 (**8**), 189186671 (**A1**) and 1891872 (**A2**) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, CambridgeCB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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