Fluorophosphoniums as Lewis acids in organometallic catalysis: application in cobalt-catalyzed carbonylation of β-lactones

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Abstract

Within the context of the development of phosphorus-based Lewis acids, we report herein the synthesis of four fluorophosphonium organic Lewis acids, with tetracarbonyl cobaltate as counter-anion: $[R_3PF]^+[Co(CO)_4]^-$ (with R = o-Tol, Cy, ^iPr, and ^tBu). These novel ion pairs were fully characterized by NMR and IR spectroscopy, elemental analysis, and, for three of them, X-ray diffraction. The catalytic activities of these ion pairs were investigated for the carbonylation of β-lactones to succinic anhydrides. $[^tBu_3PFCo(CO)_4]$ **IV** (3 mol%) afforded 91 % of succinic anhydride after 16 h at 80 °C, at a very mild pressure of 2 bar of carbon monoxide. To our knowledge, this work is the first report on using fluorophosphoniums as main-group Lewis acids in a transition metal-catalyzed reaction.

Introduction

Despite the description of syntheses and characterizations of some fluorophosphoniums since the 1960s,[1] their application as Lewis acidic catalysts only emerged recently. Indeed, since 2012,[2] the group of Stephan has reported an extensive array of fluorophosphoniums, which have contributed to the expansion of metal-free catalytic processes, for reactions such as hydrosilylation of ketones,[3] imines, nitriles, and olefins,[4] isomerization of olefins,[4b] hydrodefluorination of fluoroalkanes,[4d, 4e, 5] dehydrocoupling of silanes with amines, alcohols,[4d, 4e, 5a] acids, and thiols,[6] transfer hydrogenation of alkenes,[6] hydrodeoxygenation of ketones,[4c-e, 5a] deoxygenation of phosphine oxides,[7] Friedel-Craft dimerization,[4d, 4e, 5a] Diels-Alder reaction, or Nazarov cyclization.[8]

Encouraged by these results, we envisioned extending the use of Lewis acidic fluorophosphoniums to organometallic catalysis, and transition metal-catalyzed carbonylation was chosen as a relevant application. Indeed, ring-expanding carbonylation of heterocycles has been reported using a combination of a Lewis acid and a cobalt carbonyl species. The carbonylation of epoxides was first investigated by Alper *et al.* in 2001,[9] using various sources of cobalt carbonyl as catalyst, assisted by boronic Lewis acids ($[Co_2(CO)_8]$/PPNCl or $[PPNCo(CO)_4]$, assisted by $BF_3 \cdot Et_2O$ or $B(C_6F_5)_3$, PPN = bis(triphenylphosphine)iminium). The reaction was improved in the

following years by the group of Coates with porphyrin or salphen-based tetradentate chromium or aluminum Lewis acids to obtain unprecedented activity in the carbonylation of epoxides to lactones (Scheme 1, Cat. 1),[10] lactone to anhydride (Scheme 1, Cat. 2),[11] or the direct double carbonylation of epoxides to anhydrides (Scheme 1, Cat. 3).[12] An aluminum phthalocyanine was also reported as a suitable Lewis acid for the carbonylation of epoxides.[13] Recently, the groups of Yoon[14] and of Dincă and Román-Leshkov[15] reported supported heterogeneous catalysts based on these tetradentate chromium or aluminum Lewis acids. In these reactions, the role of the Lewis acidic cation is decisive for the activity of the catalytic system:[12] while the cation should be Lewis acidic enough to bind to the substrate and thus activate it for its ring-opening through bimolecular nucleophilic substitution by $[Co(CO)_4]^-$, it should also, after the carbonylation step, allow the final ring-closure to release the product.

Since the low-lying P–F σ* orbital of fluorophosphoniums provides them high Lewis acidity,[16] and since additional tuning can be brought through the choice of stronger or milder electron-withdrawing substituents around the phosphorus atom, these cations can be envisaged as suitable promoters for the carbonylation of heterocycles catalyzed by $[Co(CO)_4]^-$.
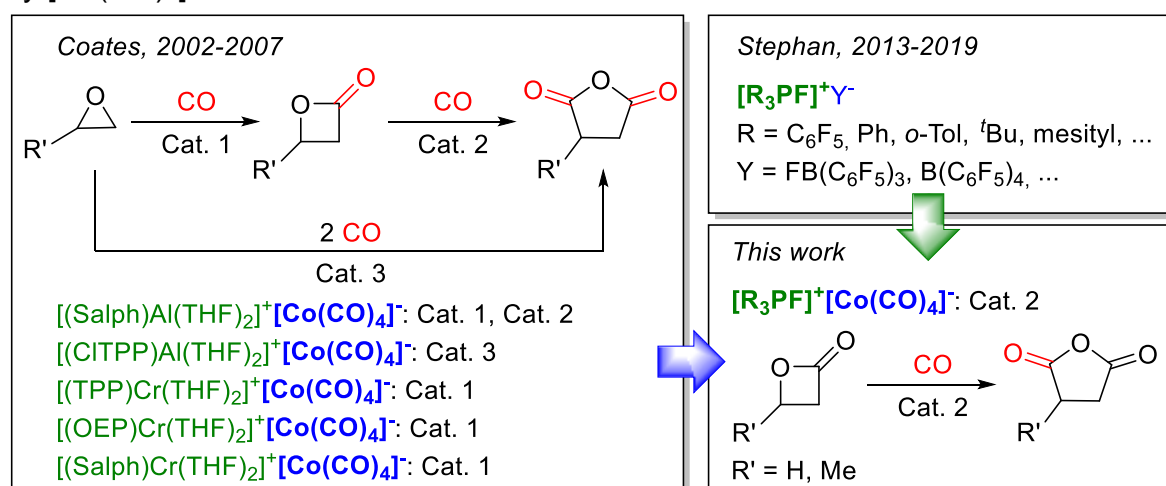
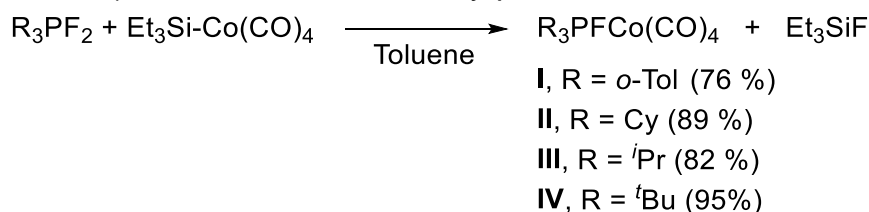Scheme 1. Left: selected examples of [Lewis acid]⁺[Co(CO)₄]⁻ ion pairs reported by the group of Coates, used as homogeneous catalysts for the carbonylation of epoxides and β-lactones. Top right: selected examples of ion pairs, including a fluorophosphonium cation, reported by the group of Stephan. Bottom right: this work, where novel [Lewis acid]⁺[Co(CO)₄]⁻ ion pairs, including a fluorophosphonium cation, are used as catalysts for the carbonylation of β-lactones to succinic anhydrides.

Therefore, we envisioned ion pairs of the formula $[R_3PF]^+[Co(CO)_4]^-$ as possible well-defined catalysts for the carbonylation of heterocycles. Although using main-group instead of metal-based Lewis acids seemed advantageous, uncertainty remained regarding their compatibility with the conditions, reactants, and substrates in carbonylations. This work aimed thus at evaluating the performances of $[R_3PF]^+$ species as Lewis acidic partners in a dual organometallic catalytic process.

Herein we report the syntheses and characterizations of four fluorophosphoniums associated with a tetracarbonyl cobaltate anion, which were then engaged in the carbonylation of β-propiolactone (PL) to succinic anhydride (SA), and of β-butyrolactone (BL) to methyl succinic anhydride (MeSA).

Results and discussion

The starting difluorophosphines were synthesized according to the literature procedure from the corresponding phosphine and XeF₂,[17] and, without purification, were reacted with an *in situ* generated triethylsilyltetracarbonylcobalt[18] in toluene to give the ion pairs **I-IV** as yellow, green, or blue powders in good to high yields after purification and isolation (Scheme 2). Et₃SiF is formed as a by-product.

$$R_3PF_2 + Et_3Si\text{-}Co(CO)_4 \xrightarrow{\text{Toluene}} R_3PFCo(CO)_4 + Et_3SiF$$

I, R = *o*-Tol (76 %)
II, R = Cy (89 %)
III, R = ^{i}Pr (82 %)
IV, R = ^{t}Bu (95%)

Scheme 2. Synthetic pathway towards fluorophosphonium tetracarbonyl cobaltates **I-IV**.

Syntheses were attempted with other aryl substituents around the phosphorus atom: whereas the ion pair [(*o*-Tol)₃PF]⁺[Co(CO)₄]⁻ **I** could be easily obtained, the syntheses of [Ph₃PF]⁺[Co(CO)₄]⁻ and [Mes₃PF]⁺[Co(CO)₄]⁻ were however unsuccessful and the products were either not stable (for R = Ph) or not forming (for R = Mes) (Mes: mesityl; see S.I., section 2.1).

The ¹⁹F and ³¹P NMR spectra of complexes **I-IV** exhibited characteristic doublets corresponding to the phosphorous-fluorine coupling (*J* ≈ 1000 Hz), with chemical shifts similar to the fluorophosphoniums reported by the groups of Schmutzler[19] or Stephan[17] with Br⁻, PhPF₅⁻, FB(C₆F₅)₃⁻ or B(C₆F₅)₄⁻ as counter-anions (Table 1).

Table 1. ¹⁹F and ³¹P chemical shifts and phosphorous-fluorine couplings exhibited by **I-IV** and similar fluorophosphoniums previously reported.

Entry	Catalyst	$J_{\text{P-F}}$ (Hz)	δ(³¹P) (ppm)	δ(¹⁹F) (ppm)
1	[*o*-Tol₃PF]⁺ [Co(CO)₄]⁻ (**I**)	993	103.19	−125.41
2ᵃ	[*o*-Tol₃PF]⁺ [FB(C₆F₅)₃]⁻	994	104.3	−125.5
3ᵃ	[*o*-Tol₃PF]⁺ [B(C₆F₅)₄]⁻	993	103.2	−125.5
4	[Cy₃PF]⁺ [Co(CO)₄]⁻ (**II**)	993	133.03	−171.09
5	[^{i}Pr₃PF]⁺ [Co(CO)₄]⁻ (**III**)	997	146.43	−169.43
6ᵇ	[^{i}Pr₃PF]⁺ Br⁻	966	145.0	−167.0
7ᵇ	[^{i}Pr₃PF]⁺ [PhPF₅]⁻	962	147.0	−167.0
8	[^{t}Bu₃PF]⁺ [Co(CO)₄]⁻ (**IV**)	1019	150.64	−171.38
9ᵃ	[^{t}Bu₃PF]⁺ [FB(C₆F₅)₃]⁻	1019	148.5	−171.6
10ᵃ	[^{t}Bu₃PF]⁺ [B(C₆F₅)₄]⁻	1019	147.5	−171.6

ᵃ From ref. 17 ᵇ From ref. 19

As described by the group of Stephan,[17] the more electron-withdrawing the substituents on the fluorophosphonium, the lower the ³¹P NMR chemical shifts, and the higher the ¹⁹F NMR chemical shifts: the aryl-substituted **I** showcase a ³¹P NMR chemical shift around 100 ppm and a ¹⁹F NMR chemical shift around –125 ppm, while for alkyl-substituted **II**, **III**, and **IV**, δ(³¹P) ≈ 140 ppm, and δ(¹⁹F) ≈ –170 ppm (Figure 1).
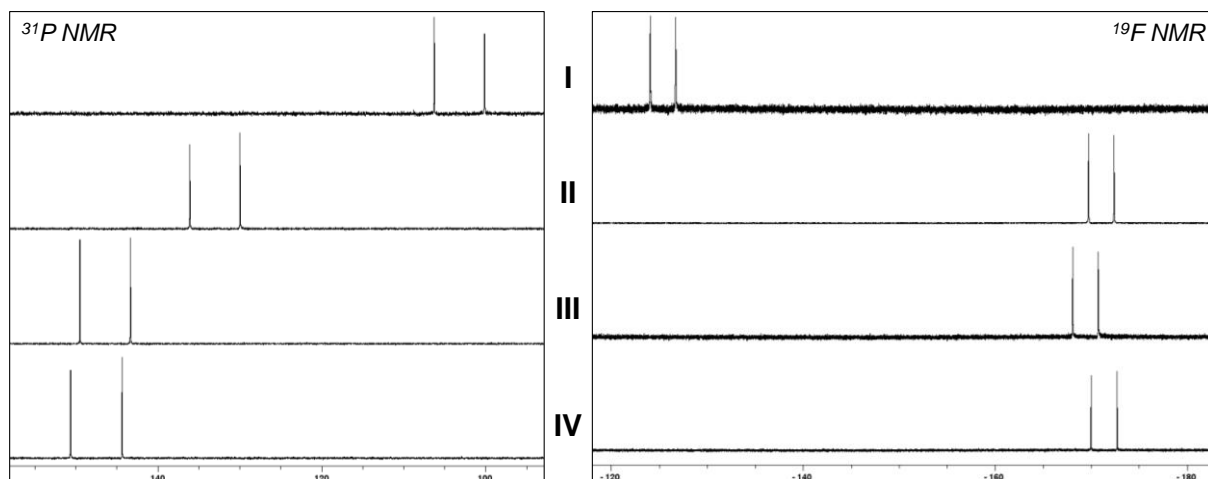
Figure 1. Stack plot of ^{31}P NMR and ^{19}F NMR spectra of **I-IV**.
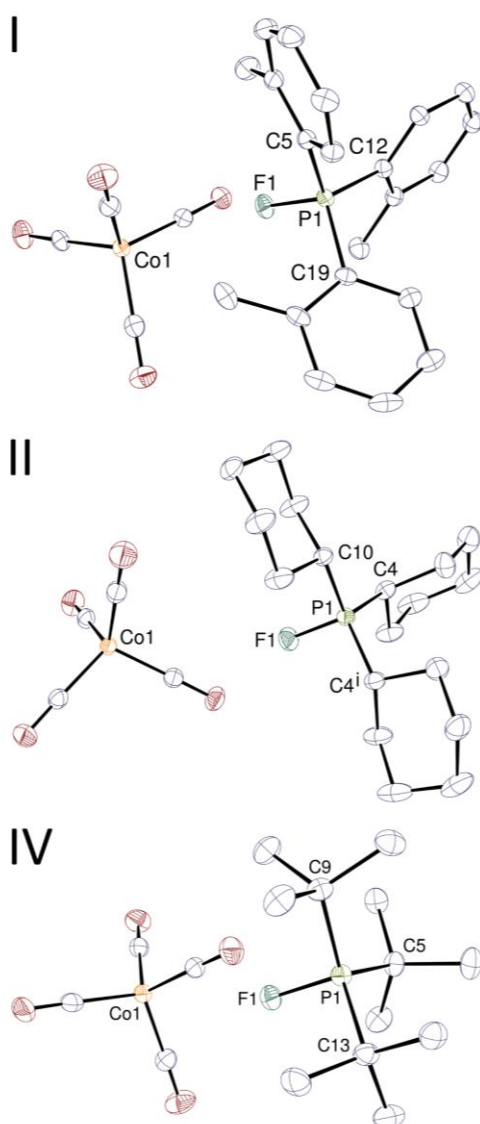
Figure 2. Crystal structures of **I**, **II** and **IV**. Displacement ellipsoids are shown at the 50% probability level and hydrogen atoms are omitted. Symmetry code for **II**: i = x, 3/2 – y, z. Selected bond distances (Å) and bond angles (°). For **I**: P1–F1 1.5486(8); C5–P1–C12 110.68(6); C5–P1–C19 114.14(6); C12–P1–C19 112.27(6). For **II**: P1–F1 1.5547(10); C4–P1–C4^i 118.57(7); C4–P1–C10 111.51(4). For **IV**: P1–F1 1.5563(9); C5–P1–C9 114.35(7); C9–P1–C13 114.97(6); C13–P1–C5 115.27(7).

Crystals of **I**, **II**, and **IV** were obtained by diffusion of pentane in a DME solution (Figure 2). The cobalt and phosphorus atoms adopt tetrahedral geometries in the molecular structure of **I**, **II**, and **IV**. While complexes **I** and **IV** are devoid of symmetry, **II** presents with mirror symmetry. The P–F bond lengths are all similar, around 1.555 Å, suggesting that the bulkiness of the substituents does not have much influence on the length of the P–F bond in our fluorophosphoniums; on the contrary, the group of Stephan[17] reported that the P–F bond length in [o-Tol$_3$PF][FB(C$_6$F$_5$)$_3$] was 1.5543(3) Å ($vs.$ 1.549(1) Å in **I**), which was significantly lower than 1.628(2) Å in [^{t}Bu$_3$PF][FB(C$_6$F$_5$)$_3$] ($vs.$ 1.5563(9) Å in **IV**). The sums of the C–P–C angles are respectively 337.1, 341.6, and 344.6 ° in **I**, **II**, and **IV**, consistent with the increasing bulkiness of the substituents on the phosphorus atom. The anion and cation are well separated, with Co–F distances of 3.5881(8), 4.3906(10), and 5.5795(8) Å in **I**, **II**, and **IV**, respectively, much larger than the sum of the ionic radii of cobalt and fluorine (ca. 1.9 Å).[20]

Table 2. Study of the catalytic activity of **I-IV** for the carbonylation of PL to SA and optimization of the reaction conditions.[a]

Entry	Catalyst	P$_{CO}$ (bar)	T (°C)	PL conversion (%)	SA yield (%)
1	**I**	50	80	74	58
2	**II**	50	80	87	75
3	**III**	50	80	88	70
4	**IV**	50	80	85	75
5	**IV**	50	100	95	74
6	**IV**	20	80	96	78
7	**IV**	10	80	99	91
8	**IV**	2	80	96	90

[a] Conditions: PL (2 mol·L^{-1}), mesitylene (internal standard, 10 mol%), and the catalyst in toluene (1 mL), heated for 16 h under CO.
SA yields and PL conversions measured by GC-MS analysis.

Fluorophosphoniums **I-IV** were engaged in the carbonylation of PL to SA (Table 2). Under 50 bar of CO, in toluene, after 16 h of reaction, whereas only 58 % of SA was obtained when aryl-substituted **I** was used as a catalyst (Table 2, entry 1), alkyl-substituted **II**, **III**, and **IV** afforded respectively 75, 70, and 75 % of SA (Table 2, entries 2 and 4). According to reports by the group of Coates on the mechanism of the carbonylation of β-lactones,[12] the rate-determining step of this reaction is the nucleophilic attack of [Co(CO)$_4$]$^-$ on the substrate, with the assistance of the Lewis acidic cation. It would then have been expected that the catalyst comprising the stronger Lewis acidic fluorophosphonium, $i.e.,$ aryl-substituted **I**, would perform the best. Nonetheless, the Lewis acid is also involved in the last step of the mechanism, where it forms an adduct with the cobalt-acyl intermediate before the ring closure.

Using a strong Lewis acidic cation would enhance the stability of this intermediate, thus slowing down the ring closure. Aryl-substituted fluorophosphonium **I** may be so Lewis acidic that it excessively stabilizes the cobalt-acyl intermediate, and therefore, the alkyl-substituted fluorophosphonium cations in **II**, **III**, and **IV**, which display milder Lewis acidity, are more suitable as counter-cations for this reaction. No significant difference in activity could be observed between **II**, **III**, and **IV**.

Further optimization was performed with catalyst **IV**: a similar yield of SA was obtained when the reaction was run at 100 °C instead of 80 °C, while the conversion of PL increased from 85 to 95 %, suggesting that a higher temperature reduced the selectivity (Table 2, entry 5). Lowering the CO pressure contributed to a better catalytic activity: 78 % of SA was obtained at 20 bar, 91 % at 10 bar, and 90 % at 2 bar, with almost complete conversion of PL in each case (Table 2, entries 6-8). Compared to the system proposed by the group of Coates, which yielded 98 % of SA from the carbonylation of PL under 14 bar of CO in the presence of $[(salph)Al(THF)_2]^+[Co(CO)_4]^-$ (0.3 mol%) after 24 h at 24 °C, our catalytic system afforded SA in high yields as well, with only low to moderate pressure of CO; however, the metallic-based LA of Coates appears to be more active, and at room temperature, since our main-group LA required the application of a higher catalytic loading and a higher temperature to achieve similar activity in a comparable duration.

Table 3. Optimization of the carbonylation of BL to MeSA, catalyzed by **IV**.[a]

Entry	T (°C)	Duration (h)	BL conversion (%)	MeSA yield (%)
1	80	16	3	4
2	100	16	33	33
3	100	48	92	72
4	120	16	74	62
5[b]	120	52	89	64
6[c]	140	16	86	28

[a] Conditions: BL (2 mol·L^{-1}) and mesitylene (internal standard, 10 mol%) with **IV** (3 mol%) in toluene (1 mL), heated for the indicated duration under CO (10 bar). MeSA yields and BL conversions measured by GC-MS analysis. [b] 9 % of CA was obtained as a side-product. [c] 49 % of CA was obtained as a side-product.

The same reaction conditions were applied to the more challenging carbonylation of BL to MeSA catalyzed by **IV** (Table 3). The presence of the methyl group hinders the electrophilic site of the lactone and causes the rate-determining ring-opening of BL by nucleophilic attack of $[Co(CO)_4]^-$ to be more difficult,[12] and indeed, only traces of MeSA were obtained after 16 h at 80 °C, under 10 bar of CO (Table 3, entry 1). Providing more energy to the system thanks to elevated reaction temperatures unlocked the activity of the catalytic system: 33 % of MeSA was afforded after 16 h at 100 °C, 62 % at 120 °C, but only 28 % at 140 °C (Table 3, entries 2, 4, and 6). Nonetheless, higher temperatures induced a reduction of the selectivity as well: CO_2 and H_2 were detected

in the gas phase after carbonylation runs at 100, 120, or 140 °C (see S.I., section 3.2), while isomerization of BL to crotonic acid was observed at 140 °C, and even at 120 °C after a prolonged heating (Table 3, entries 5, and 6). This suggests that a compromise should be found in the choice of temperature between activation and selectivity. Still, the 48-hour-long reaction at 100 °C enabled the almost complete conversion of BL and yielded 72 % of MeSA (Table 3, entry 3).

Conclusion

In summary, we described the synthesis and characterization of four fluorophosphonium tetracarbonyl cobaltates. The investigation of the catalytic activities of **I-IV** in the carbonylation of PL to SA showed that alkyl-substituted catalysts were the best candidates, and further optimization demonstrated that **IV** catalyzed the carbonylation of PL and BL to respectively SA and MeSA in good to high yields at low pressure. To the best of our knowledge, this is the first report of using fluorophosphoniums as organic Lewis acids in a transition metal-catalyzed reaction.

Acknowledgments

Supplementary Data

Electronic supplementary information (ESI) available: synthetic procedures, characterization details, and analytic details. Deposition numbers 2286472–2286474 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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