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The $Pd_3(dppm)_3(CO)^{2+}$ Cluster: An Efficient Electrochemically Assisted Lewis Acid Catalyst for the Fluorination and Alcoholysis of Acyl Chlorides

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Abstract: The dicationic palladium cluster $Pd_3(dppm)_3(CO)^{2+}$ (dppm = bis(diphenylphosphino)methane) reacts with acid chlorides RCOCl (R = n-C_6H_{13}, t-Bu, Ph) to afford quantitatively the chloride adduct $Pd_3(dppm)_3(CO)(Cl)^+$ and the acyl cation RCO^+ as the organic counterpart. The dicationic reactive cluster can be reformed by electrolyzing the chloride complex with a copper anode leaving CuCl as a byproduct. The combination of these two reactions provides an electrocatalytic way to form the acylium from the acid chloride. Indeed, in CH_2Cl_2, 0.2 M NBu_4PF_6, or NBu_4BF_4, the electrolysis of the acid chloride in the presence of a catalytic amount of the cluster (1%) gives in good yields the acid fluoride RCOF, arising from the coupling of the acylium with a F^- issued from the fluorinated supporting electrolyte. Alternatively, in CH_2Cl_2 or 0.2 M NBu_4ClO_4, by operating with an alcohol R′OH as the nucleophile, the electrolysis gives the ester RC(O)OR′ as the only final product.

The importance of palladium in hetero- and homogeneous catalysis is well-known.[2] However, electrocatalytic systems are rather uncommon. Recently, it was shown that the great affinity of $Pd_3(dppm)_3(CO)^{2+}$ (Pd_3^{2+})[3] toward halide ions promotes the heterolytic cleavage of the C−X (X = Br, I) bond of alkyl halides (eq 1).[4] The detailed analysis of the mechanism implies an electrochemical induction leading to an electron-transfer chain reaction. The driving force for this reaction is the great stability of the $Pd_3(dppm)_3(CO)(X)^+$ inorganic product (Pd_3X^+).[5] Hence, the formation of "R^+" provides an opportunity to seek applications. As an example, the latter species can be trapped with phenol, as a nucleophile, to generate the corresponding nonsymmetric ether.

$$Pd_3(dppm)_3(CO)^{2+} + RX \rightarrow Pd_3(dppm)_3(CO)(X)^+ + \text{“}R^+\text{”} \quad (1)$$

$$R = Me,\ Et,\ {}^iPr,\ {}^nBu,\ {}^tBu,\ Bz,\ PhCH_2CH_2;\ X = Br,\ I$$

To render this process catalytic, one has to address the challenging problem of the regeneration of the Pd_3^{2+} species. To abstract the halide from the Pd_3^{2+} center, another Lewis acid must be used that can cleanly and irreversibly eliminate these ions in a way that no side or competitive reaction occurs.

Acyl chlorides react more rapidly than RX with Pd_3^{2+} and do not need electrochemical induction. This reaction is the same as in the RX cases, except that, instead of a carbonium, an acylium intermediate "RCO^+" is generated. By trapping this cation with a selected nucleophile, the reaction can be directed toward the formation of desired products. This paper reports two applications: the fluorination and the alcoholysis of acid chlorides.

Catalysis Design. The Pd_3^{2+} cluster reacts with the acid chlorides RC(O)Cl (R = Ph, n-C_6H_{13}, t-Bu) to generate quantitatively Pd_3Cl^+ [6] product (eq 2):

$$Pd_3(dppm)_3(CO)^{2+} + RC(O)Cl \rightarrow Pd_3(dppm)_3(CO)(Cl)^+ + \text{“}RCO^+\text{”} \quad (2)$$

The stoechiometric addition of $Cu(NCMe)_4^+$, a reagent commonly employed for Cl^- abstraction,[7] provides an opportunity to regenerate Pd_3^{2+} and to render reaction 2 catalytic. Indeed, this reaction proceeds quantitatively (reaction 3):

$$Pd_3(dppm)_3(CO)(Cl)^+ + Cu(CH_3CN)_4^+ \rightarrow Pd_3(dppm)_3(CO)^{2+} + CuCl_{(s)} + 4CH_3CN \quad (3)$$

The latter requires the use of $Cu(NCMe)_4^+$, which needs to be synthesized at a prior stage. Instead, in a more practical way, reaction 3 can also proceed quantitatively, but in one step by means of electrolysis of the Pd_3Cl^+ solution with a copper anode as the working electrode (polarized at +0.65 V versus SCE). Coulometric measurements indicate that 1 F/mol of Pd_3Cl^+ is required to regenerate Pd_3^{2+}:

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[2] For recent published works, see: (a) Tsuji, J. *Palladium Reagents amd Catalysts*; Wiley: New York, 1995. (b) Moiseev, I. I.; Vargaftik, M. N. *New J. Chem.* **1998**, *22*, 1217. (c) Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.* **2000**, *100*, 3009. (d) Shmid, G. *Clusters and Colloïds*; VCH: Weinheim, 1994. (e) Moiseev, I. I.; Vargaftik, M. N. In *Catalysis by Di- and Ploynuclear Metal Cluster Complexes*; Adams, R. D., Cotton, F. A., Eds.; Wiley-VCH: New York, 1998; Chapter 12 p 395.

[3] Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W. *Polyhedron* **1990**, *9*, 2767 and references therein.

[4] Brevet, D.; Lucas, D.; Cattey, H.; Lemaître, F.; Mugnier, Y.; Harvey, P. D. *J. Am. Chem. Soc.* **2001**, *123*, 4340.

[5] (a) The binding constants have been measured spectroscopically (X = I, Br, Cl) and electrochemically (X = I) and were found to be very large.[5b,c] (b) Harvey, P. D.; Hierso, K.; Braunstein, P.; Morise, X. *Inorg. Chim. Acta* **1996**, *250*, 337. (c) Lemaître, F.; Brevet, D.; Lucas, D.; Vallat, A.; Mugnier, Y.; Harvey, P. D. *Inorg. Chem.* **2002**, *41*, 2368.

[6] (a) The Pd_3Cl^+ was identified from its ^{31}P NMR spectrum and cyclic voltammogram (CV) by comparison with an authentic sample.[6b] (b) The complex Pd_3Cl^+ has been prepared according to the literature method;[3] the ^{31}P NMR and electrochemical data are as follows: δ (acetone-d_6) = −6.53 ppm and $E_{1/2}{}^{2+/0}$ = −0.77 V vs SCE (in THF 0.2 M of Bu_4NPF_6).

[7] (a) Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90. (b) Braunstein, P.; Luke, M. A. *New J. Chem.* **1988**, *12*, 429. (c) Braunstein, P.; Luke, M. A.; Tiripicchio, A.; Camellini, M. *Angew. Chem., Int. Ed. Eng.* **1987**, *26*, 768.

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$$\mathrm{Pd_3(dppm)_3(CO)(Cl)^+ + Cu - e^- \rightarrow Pd_3(dppm)_3(CO)^{2+} + CuCl_{(s)}} \quad (4)$$

Combining reactions 2 and 4 provides the catalytic cycle depicted in Scheme 1, which results in the selective formation of the acylium cation from the acyl chloride.

The overall reaction can be written as follows (eq 5), where the precipitation of CuCl constitutes the driving force of the whole process:

$$\mathrm{RC(O)Cl + Cu_{(s)} - e^-} \xrightarrow{\mathrm{Pd_3}^{2+}\text{(cat.)}} \text{“}\mathrm{RCO^+}\text{”} + \mathrm{CuCl_{(s)}} \quad (5)$$

As a typical example, when the Pd_3^{2+} is introduced into the solution together with an excess of acid chloride (100 molar equiv), using various derivatives (such as R = Ph, *t*-Bu, or *n*-C_6H_{13}), polarizing the copper electrode generates a strong current, which indicates an increase of electron flow. The latter drops to zero after the quantity of current passed has nearly reached the amount of acid chloride initially introduced. The CuCl produced throughout the electrolysis was quantified, giving a quantitative yield with respect to the electrolyzed acid chloride.[8] This catalytic system can be of great utility in acylation reactions. Two synthetic applications are selected: the synthesis of fluoro acid,[9] and conversion of alcohols in esters via O-acylation.[10]

SCHEME 1

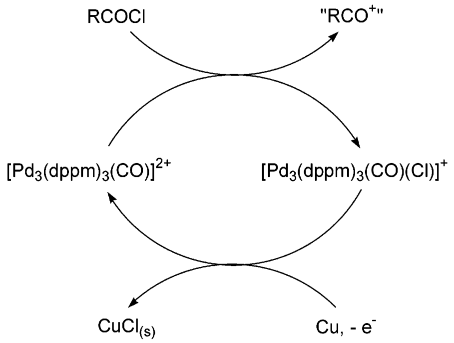

TABLE 1. Fluorination (Entries 1−4) and Alcoholysis (Entries 5−12) of Acid Chlorides Catalyzed by Pd_3^{2+} (1% Mol) under Oxidation with a Copper Anode[a]

entry	acid chloride	nucleophile	Q^b (F/mol)	chemical yield[c] (%)	faradic yield[d] (%)
1	PhCOCl	Bu_4NPF_6	0.98	98	100
2	PhCOCl	Bu_4NBF_4	0.90	86	96
3	*t*-BuCOCl	Bu_4NBF_4	0.88	86	98
4	*n*-C_6H_{13}COCl	Bu_4NPF_6	0.89	86	97
5	PhCOCl	MeOH	0.88	84	95
6	PhCOCl	EtOH	0.84	78	93
7	*t*-BuCOCl	EtOH	0.85	80	94
8	*n*-C_6H_{13}COCl	EtOH	0.93	85	91
9	PhCOCl	*i*-PrOH	0.81	80	99
10	PhCOCl	*sec*-BuOH	0.84	80	95
11	PhCOCl	*t*-BuOH	0.86	0[e]	0[e]
12	PhCOCl	*t*-BuOH	0.81	78[f]	96[f]

[a] See the general procedure in the Experimental Section. [b] Determined per mol of RCOCl, after the current had dropped to zero; the nonstoichiometric amount of electricity (relative to the quantity of acid chloride) can be explained by the passivation of the copper anode, which appears at the end of the electrolysis, recovered with cuprous chloride. [b] Determined by GC/MS (internal standard method). [d] Faradic yield = chemical yield/Q. [e] No more ester was found when the same experiment was conducted with excess alcohol (10 equiv relative to PhCOCl). [f] Conducted in an undivided cell.

Fluorination. These compounds find numerous important applications in organic synthesis.[9,11] Generally, acid fluorides are prepared from halide exchange with the corresponding acid chloride[12] with the use of a fluorinating agent such as KF,[13] KF/HF,[14] HF,[15] SbF_3,[16] BrF_3,[17] and ZrF_2.[18] These reactions require high temperature, which is rather inconvenient for polyfunctional systems. No catalyst is known for such a reaction.

By using a fluorinated supporting electrolyte, i.e., Bu_4NPF_6 (Table 1, entries 1 and 4) or Bu_4NBF_4 (Table 1, entries 2 and 3), the acid chloride is readily and quantitatively converted into the corresponding fluoride (Table 1 and eq 6):

$$\mathrm{R(C)Cl} + \text{“}\mathrm{F^-}\text{”} + \mathrm{Cu - e^-} \xrightarrow[\substack{\mathrm{CH_2Cl_2} \\ \mathrm{0.2M\ Bu_4NPF_6\ or\ Bu_4NBF_4}}]{\text{cat.: } \mathrm{Pd_3}^{2+}\ (1\%)} \mathrm{RC(O)F + CuCl_{(s)}} \quad (6)$$

The proposed mechanism involves the abstraction of a F^- from the PF_6^- or BF_4^- anion by the strongly electrophilic acylium ion.[19]

Alcoholysis. The conversion of alcohols into esters is of fundamental importance in organic synthesis.[10] The

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(8) As a blank experiment, we have verified that no current was detected when the Pd_3^{2+} was not present in solution, other conditions being unchanged. All in all, Pd_3^{2+} acts as an halide-transfer agent from the organic molecule to the electrode.

(9) (a) Carpino, L. A.; Sadat-Aalaee, H. G.; Chao, H. G.; Deselms, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 9651. (b) Bertho, J. N.; Loffet, A.; Pinel, C.; Reuther, F.; Sennyey, G. *Tetrahedron Lett.* **1991**, *32*, 1303. (c) Wenschuh, H.; Beyermann, M.; Krause, E.; Brudel, M.; Winter, R.; Schümann, M.; Carpino, L. A., Bienert, M. *J. Org. Chem.* **1994**, *59*, 3275.

(10) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; Vol. I, 475.

(11) (a) Ramig, K.; Kudzma, L. V.; Lessor, R. A.; Rozov, L. A. *J. Fluorine Chem.* **1999**, *94*, 1 and references therein. (b) Hudlicky, M.; Pavlath, A. E. *Chemistry of Organic Fluorine Compounds II: A Critical Review*; American Chemical Society: Washington, DC, 1995.

(12) (a) Hasek, W. R.; Smith, W. C.; Engelhardt, V. A. *J. Am. Chem. Soc.* **1960**, *82*, 543. (b) Bloshchitsa, F. A.; Burmakov, A. I.; Kunshenko, B. V.; Alekseeva, L. A.; Yagupol'skii, L. M. *J. Org. Chem. USSR* (Engl. Trans.) **1985**, *21*, 1286. (c) Ritter, S. K.; Hill, B. K.; Odian, M. A.; Dai, J.; Noftle, R. E.; Gard, G. L. *J. Fluorine Chem.* **1999**, *93*, 73.

(13) (a) Saunders: S. *J. Chem. Soc.* **1948**, 1778. (b) Haszeldine N. *J. Chem. Soc.* **1959**, 1084. (c) Pittman, A. G.; Sharp, D. L. *J. Org. Chem.* **1966**, *31*, 2316. (d) 18-Crown-6 complex: Liotta, C. L.; Harris, H. P. *J. Am. Chem. Soc.* **1974**, *96*, 2250. (e) Ishikawa, N.; Kitazume, T.; Yamazaki, T.; Mochida, Y.; Tatsuno, T. *Chem. Lett.* **1981**, 761. (f) Tordeux, M.; Wakselman, C. *Synth. Commun.* **1982**, *12*, 513. (g) Clark, J. H.; Hyde, A. J.; Smith, D. K. *J. Chem. Soc., Chem. Commun.* **1986**, *10*, 791. (h) Liu, H.; Wang, P.; Sun, P. *J. Fluorine Chem.* **1989**, *43*, 429. (i) Krespan, C. G.; Dixon, D. A. *J. Org. Chem.* **1991**, *56*, 3915.

(14) (a) Olah G. A.; Kuhn, S.; Beke, S. *Chem. Ber.* **1956**, *89*, 862. (b) Miller, J.; Ying, O.-L. *J. Chem. Soc., Perkin Trans. 2* **1985**, 325.

(15) (a) Young, D. *J. Org. Chem.* **1959**, *24*, 1021. (b) Olah, G. A.; Welch, J. T.; Vankar, Y. D.; Nojima, M.; Kerekes, I.; Olah, J. A. *J. Org. Chem.* **1979**, *44*, 3872. (c) Abe, T.; Hayashi, E.; Baba, H.; Nagase, S *J. Fluorine Chem.* **1984**, *25*, 419.

(16) Meerwein, H.; Borner, P.; Fuchs, O.; Sasse, H. J.; Schrodt, H.; Spille, J. *Chem. Ber.* **1956**, *89*, 2060.

(17) Rozen, S.; Ben-David, I. *J. Fluorine Chem.* **1996**, *76*, 145.

(18) (a) Blicke, F. F. *J. Am. Chem. Soc.* **1924**, *46*, 1516. (b) Swain, S. *J. Am. Chem. Soc.* **1953**, *75*, 246. (c) Nenajdenko, V. G.; Lebedev, M. V.; Belenkova, E. S. *Tetrahedron Lett.* **1995**, *36*, 6317.

(19) (a) Jordan, R. F., Dasher, W. E., Echols, S. F. *J. Am. Chem. Soc.* **1986**, *108*, 1718. (b) Bochmann, M., Wilson, L. M. *Organometallics* **1987**, *6*, 2556. (c) Gorell, I. B., Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452.

acylating agent may be the acid chloride or the corresponding anhydride, as shown by eq 7:

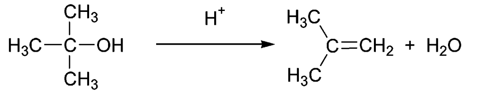
$$\begin{array}{l} RC(O)Y + R'(OH) \rightarrow RC(O)OR' + HY \\ Y = Cl, OC(O)R \end{array} \qquad (7)$$

The most popular catalyst used for this reaction is 4-(dimethylamino)pyridine (DMAP), which needs the presence of a base, generally a tertiary amine.[20] The drawback is that the quantity of required catalyst is comparatively great (5−10%) instead of 1% commonly used and the amine cocatalyst is in excess. In addition, DMAP is uneffective toward sterically hindrered alcohols. Occasionally, high temperature, long reaction time, and an excess of acyl reactants are necessary. This situation has led over the past 10 years to the development of various catalysts, including $TaCl_5$,[21] TMSOTf,[22] $Sc(OTf)_3$,[23] Bu_3P,[24] $CoCl_2$,[25] Montmorillonite K-10, and KSF,[26] and inorganic solids such as alumine[27] and zinc.[28] By combining Bu_4NClO_4 as a nonreactive supporting electrolyte and an alcohol as the nucleophile, our catalytical method allows one to obtain in good yield the corresponding disymmetric ester (Table 1 and eq 8):

$$R(CO)Cl + R'OH + Cu - e^- \xrightarrow[\substack{CH_2Cl_2 \\ 0.2\ M\ Bu_4NClO_4}]{\text{cat.: } Pd_3^{2+}\ (1\%)} R(CO)OR' + CuCl_{(s)} + H^+ \qquad (8)$$

The results are summarized in Table 1. With a wide range of type of alcohols and acid chlorides, the reaction is found to be in the range of 78−85% while the faradic yield is close to 100%.

The yield is high, even with sterically encumbered reactants such as pivaloyl chloride (Table 1, entry 7) or *tert*-butyl alcohol (Table 1, entry 12). In these cases, the reaction can be thwarted by a side reaction involving the released proton in reaction 8 (eq 9).[29]



(9)

To solve this problem, the use of a platinum cathode in the same compartment prevents the undesired reaction by forcing the reduction of H^+ as soon as it is formed, thus giving the ester as the sole product (Table 1, entry 12). On the other hand, when the electrolysis proceeds in a double-compartment cell, the reaction does not produce the ester, presumably forming the alkene (Table 1, entry 11). This point will be investigated further.

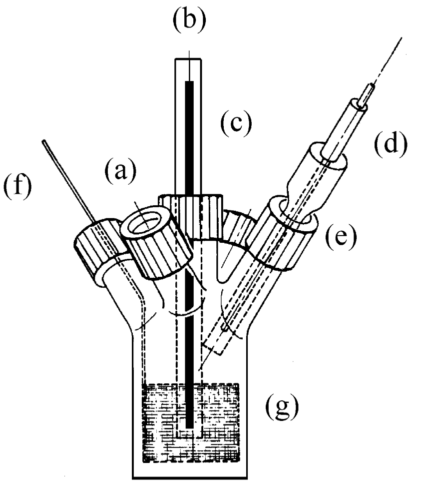


FIGURE 1. Diagram of the electrochemical cell: (a) argon inlet; (b) platinum counter-electrode; (c) tube with sintered glass cap to separate the counter-electrode from the other compartments; (d) saturated calomel reference (reference electrode); (e) tube with sintered glass cap to isolate the aqueous phase reference electrode; (f) electrical copper wire; (g) copper plate (working electrode; anode).

In conclusion, both alcoholysis and fluorination operate under particularly mild conditions (room temperature, small quantity of catalyst, and no excess of reactant). This important feature leaves hope that this method can selectively transform sensitive and polyfunctional molecules. In addition, this method is also potentially useful to any other acylation reaction. Indeed, recent experiments have demonstrated that it is active in Friedel−Crafts catalysis. Studies are currently in progress.

Experimental Section

Materials. The $[Pd_3(dppm)_3(CO)](PF_6)_2$ complex has been prepared according to the literature procedure.[3] Dichloromethane was distilled under Ar over P_2O_5. The Bu_4NPF_6 salt was synthesized by mixing stoichiometric amounts of Bu_4NOH (40% in water) and HPF_6 (60% in water). After filtration, the salt was recrystallized twice in ethanol and dried at 80 °C for at least 2 days.

Electrochemical Experiments. All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon gas. The supporting electrolyte was degassed under vacuum before use and then solubilized at a concentration of 0.2 M. High-scale[30] electrolyses were performed with an Amel 552 potentiostat coupled with an Amel 721 electronic. A copper plate was used as the working electrode (anode), a platinum plate as the counter-electrode (cathode), and a saturated calomel electrode as the reference electrode, each one being separated from the others in a three-compartment cell (Figure 1, except the last experiment of Table 1 as described in the text).

Typical Procedures. Conversion of Acid Chlorides into Esters: Preparation of Ethyl Benzoate. The $[Pd_3(dppm)_3$-

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(20) (a) Hofle, G.; Steglich, W.; Vorbruggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569. (b) Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *12*, 129.

(21) Chandrasekhar, S.; Ramachander, T.; Takhi, M. *Tetrahedron Lett.* **1998**, *39*, 3263.

(22) (a) Procopiou, P. A.; Baugh, S. P. D.; Flack, S. S.; Inglis, G. G. A. *Chem. Commun.* **1996**, 2625.. (b) Procopiou, P. A.; Baugh, S. P. D.; Flack, S. S.; Inglis, G. G. A. *J. Org. Chem.* **1998**, *63*, 2342.

(23) (a) Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1995**, *117*, 4413. (b) Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4560. (c) Ishihara, K.; Kubota, M.; Yamamoto, H. *Synlett* **1996**, 265. (d) Barett, A. G. M.; Braddock, D. C. *Chem. Commun.* **1997**, 351. (e) Zhao, H.; Pendri, A.; Greenwald, R. B. *J. Org. Chem.* **1998**, *63*, 7559.

(24) (a) Vedejs, E.; Diver, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 3358. (b) Vedejs, E.; Benett, N. S.; Conn, L. M.; Diver, S. T.; Gingras, M.; Oliver, P. A.; Peterson, M. J. *J. Org. Chem.* **1993**, *58*, 7286.

(25) Iqbal, J.; Srivastava, R. R. *J. Org. Chem.* **1992**, *57*, 2001.

(26) (a) Li, A.-X.; Li, T.-S., Ding, T.-H. *Chem. Commun.* **1997**, 1389. (b) Bhaskar, P. M.; Loganathan, D. *Tetrahedron Lett.* **1998**, *39*, 2215.

(27) Nagasawa, K.; Yoshitake, S.; Amiya, T.; Ito, K. *Synth. Commun.* **1990**, *20*, 2033.

(28) Yadav, J. S.; Reddy, G. S.; Suinivas, D.; Himabindu, K. *Synth. Commun.* **1998**, *28*, 2337.

(29) Kaiser, E. M., Woodruff, R. A. *J. Org. Chem.* **1970**, *35*, 1198.

(30) In analytical electrochemistry, the concentration of the analytes is nearly 10^{-3} M, whereas it is close to 10^{-1} M in high-scale electrolyses.

(CO)]$(PF_6)_2$ cluster (15.8 mg, 8.82×10^{-3} mmol, 1 mol % per mol of acyl chloride), ethanol (51 μL, 0.87 mmol), and benzoyl chloride (100 μL, 0.86 mmol) were added to the anodic compartment of the cell containing 15 mL of a 0.2 M solution of Bu_4NClO_4 in CH_2Cl_2. The cathodic compartment and the reference electrode compartment were filled with the Bu_4NClO_4–CH_2Cl_2 solution. The potential of the copper anode was set to +0.65 V vs SCE. The electrolysis was stopped after the current had dropped to less than 0.5 mA. After filtration of the mixture, the solvent was evaporated and the residue extracted with ether (3 × 5 mL). The internal standard method was used to measure the GC yield of the ester product. The latter was identified by comparison of the GC–MS spectra and GC retention times to those of available authentic samples.

Fluorination of Acid Chlorides. The procedure is the same as described above, except that no alcohol is added and Bu_4NPF_6 or Bu_4NBF_4 is used instead of Bu_4NClO_4.

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