A New, Highly Selective Rh(III) Catalytic System for Carboxylation of Arenes via C–H Activation under Mild Conditions**

Vladimir V. Grushin,* William J. Marshall, David L. Thorn*

Central Research and Development, E. I. DuPont de Nemours & Co., Inc., Experimental Station, Wilmington, Delaware 19880–0328, USA
Fax: (+1) 302-695-8281; e-mail: vlad.grushin-1@usa.dupont.com

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While considerable progress has been made in the field of C–H activation with transition metal complexes,[1] the number of potentially useful metal-catalyzed C–H functionalization reactions remains rather limited.[2] One transformation of this kind is the Fujiwara reaction which affords aromatic carboxylic acids directly from arenes and CO (Scheme 1).[3]

$$\mathrm{PhH} + \mathrm{Pd(OAc)_2} + \mathrm{CO} + \mathrm{H_2O} \longrightarrow \mathrm{PhCOOH} + \mathrm{Pd} + 2\mathrm{AcOH}$$

Scheme 1.

Originally stoichiometric in $Pd(OAc)_2$,[4] the Fujiwara reaction can be rendered catalytic in Pd if run in the presence of oxidants capable of converting the Pd(0) back to the active Pd (II) form.[5] Of special interest is the oxidative carbonylation of toluene as a new route to *p*-toluic acid, a precursor for terephthalic acid and other bifunctionalized arenes which find numerous large-scale industrial applications.[6] However, the catalytic turnover numbers (TON = mol product/mol catalyst) achieved for the Pd-catalyzed Fujiwara carbonylation of toluene are usually low (2–8) and the *para*-selectivity of the reaction never exceeded 67%, normally being in the range of 40–55%.[5] Better *p*-selectivities (63–94%) have been reported for the oxidative carbonylation of toluene in the presence of homogeneous[7,8] and heterogeneous[7] Rh catalysts. These Rh-catalyzed reactions, however, require high temperatures (140–150 °C) and pressures (10–270 atm)[7,8] and may be not free from safety concerns.[9] It was not clear if the drastic conditions were needed for the C–H activation or for $Rh^+ \rightarrow Rh^{3+}$ re-oxidation. In this paper we report a homogeneous Rh catalytic system for the preparation of aromatic carboxylic acids directly from corresponding arenes under very mild conditions, i. e., 20–65 °C and P_{CO} = 1 atm, with selectivities to *p*-toluic acid from toluene being 93–98%. Evidence is also presented for the re-oxidation step rather than C–H activation being rate limiting.

We found that exhaustive oxidation of $[Rh(CO)_2(CF_3CO_2)]_n$ (Figure 1)[10] with 30% H_2O_2 in CF_3COOH (TFAH) afforded a carbonyl-free (IR), orange amorphous material, "$[Rh(TFA)_3]$", which exhibited exceptional catalytic activity for aromatic C–H activation.[11] Thus, facile H/D exchange readily occurred at 20 °C between TFAH and benzene-d_6 or toluene-d_8 (hundreds of turnovers/day). When toluene-d_8 was used, the exchange occurred exclu-

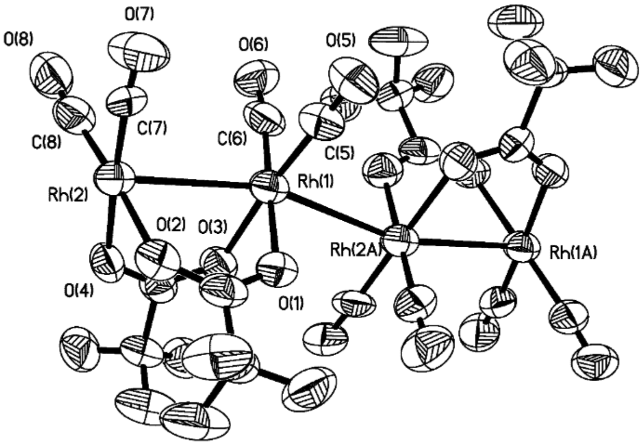

Figure 1. Molecular structure of $[Rh(CO)_2(CF_3CO_2)]_n$ (ORTEP). Selected bond distances [Å] and angles [°]: Rh1–Rh2 2.974(3), Rh1–Rh2A 3.080(3), Rh1–C5 1.823(15), Rh1–C6 1.844(17), Rh1–O1 2.081(10), Rh1–O3 2.082(9), Rh2–C7 1.807(15), Rh2–C8 1.801(17), Rh2–O2 2.028(11), Rh2–O4 2.091(9), Rh2–Rh1–Rh2 A 161.52(4), Rh1–Rh2 A–Rh1 A 163.44(4), Rh–C–O 174.1–177.9 (14–15).

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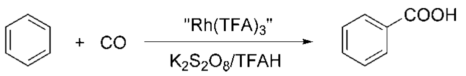
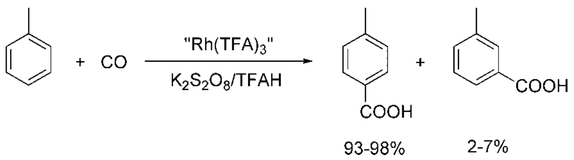
sively at the *para* and *meta* positions with > 70% *p*-selectivity. A more accurate determination of the *p*-selectivity by NMR is impeded by multiple H/D exchange and the kinetic isotope effect observed (see below). Importantly, neither the CD_3 group nor *ortho*-CD bonds were involved in the exchange.

Stirring a 1 : 1 (v/v) mixture of benzene and TFAH containing $K_2S_2O_8$ and catalytic quantities of "[Rh(TFA)$_3$]" under CO (1 atm) at room temperature, led to the chemospecific formation of benzoic acid in the amount of 40 equivalents per Rh after two days (Scheme 2).



Scheme 2.

Similarly, toluene was converted to a mixture of *para*- and *meta*-toluic acids with 93–98% *para*-selectivity, yielding 35–100 equivalents of TolCOOH per Rh (Scheme 3). Yields as high as 70% on the oxidant were obtained.



Scheme 3.

The reaction of Scheme 3 also produced trace amounts of 2- and 4-$MeC_6H_4CH_2Ph$ (GC-MS). As was shown by separate experiments, the methyldiphenylmethanes are formed even in the absence of Rh via an independent side reaction, presumably involving oxidation of toluene to the radical-cation. This side-process can be easily suppressed by lowering the TFAH to toluene ratio from 1 to 0.2 and below. However, lower concentrations of TFAH relative to toluene slowed down the Rh-catalyzed carbonylation. In a similar manner, mesitylene, *p*-xylene, and naphthalene were selectively converted to $Me_3C_6H_2COOH$, $Me_2C_6H_3COOH$, and 2-$C_{10}H_7COOH$, respectively (see the Experimental Section). Remarkably, the oxidative carbonylation of naphthalene occurred with 97% β-selectivity. No reaction was observed when all experiments were repeated with AcOH instead of TFAH.[12,13]

Most studies of the Rh-catalyzed oxidative carbonylation reaction were conducted with toluene as the substrate. The reaction exhibited a number of striking features. It was found that lowering the catalyst concentration increased its lifetime and activity, leading to a considerable improvement in TON. For instance, when $[Rh] = 1.7\times10^{-3}$, 5.3×10^{-3}, 1.7×10^{-2}, and 5.5×10^{-2} M the TONs after 70 hours at room temperature were 71, 40, 10, and ca. 1, respectively. In another series of experiments, the same trend was observed when the reaction was run at 60 °C (Figure 2). Furthermore, when P_{CO} was increased from 1 to 6 atm the yield of toluic acid was ca. 30% lower, other things being equal. Hence, *lower* CO pressure and *lower* Rh concentrations *benefit* the catalysis. In independent experiments, potassium bisulfate and toluic acid did not significantly inhibit the catalytic reaction. The catalytic reaction also easily tolerated small amounts of water (1–3% of the total volume), although when moisture was present small amounts of CO_2 formed due to the water-gas shift reaction. On the contrary, the presence of a water scavenger, $(CF_3CO)_2O$, slowed down the reaction. In the range of 25 to 65 °C, the *para*-selectivity was temperature-independent, remaining consistently high (93–98%).

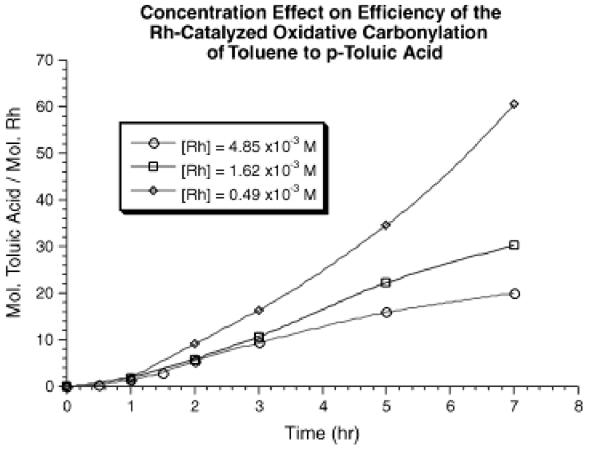


Figure 2. Catalyst concentration effect on efficiency of toluene oxidative carbonylation. Reaction conditions: TFAH (5 ml), toluene (5 mL), $K_2S_2O_8$ (2.1 g), CO (1 atm), 60 °C. Samples (0.25–1.00 mL) of the reaction mixtures were evaporated and analyzed by ^{1}H NMR in $CDCl_3$ with 1,2-dichloroethane as an internal standard.

As originally proposed for the Pd-mediated Fujiwara reaction,[3–5] the first step of the Rh-catalyzed oxidative carbonylation (Schemes 2 and 3) is probably of the S_EAr type. A number of observations support the electrophilic metalation mechanism, i. e., (i) preferential attack at the *para* site for both the H/D exchange and carbonylation reactions; (ii) the lack of catalytic activity in more strongly coordinating AcOH;[12] (iii) inhibition of both the H/D exchange (see above) and the carbonylation reaction in the presence of Cl^- due to the formation of less electrophilic chlororhodium species;[14] (iv) the kinetic isotope effect for the toluene carbonylation reaction, $k_H/k_D = 3$,[15] characteristic of S_EAr reactions involving metal[1] or bulky electrophiles under strongly acidic conditions;[16,17] (v) the carbonylation rate constant ratio $k_{TolH}/k_{PhH} = 2.1$[18] being close to the value of 1.7 previously measured for the S_EAr nitration reactions of benzene and toluene.[16]

Once formed, the Ar–Rh bond may undergo migratory insertion of CO, followed by nucleophilic cleavage of the acyl intermediate by water or TFAH to produce the aromatic carboxylic acid or its mixed anhydride derivative, and Rh(I).[19] The latter must be oxidized back to Rh(III) before another catalytic turnover can be initiated. This Rh(I) to Rh(III) oxidation step appears to be the bottleneck of the process.[20] In the reaction environment, Rh(I) carbonyl TFA species equilibrate with $[(\text{arene})Rh(CO)_2]^+$ that may be less prone to oxidation than $[Rh(CO)_2(CF_3CO_2)]_n$. In TFAH/toluene, however, the arene complex is present only in low concentrations.[21] Apparently more harmful for the catalysis is the formation of $[Rh_2(TFA)_4]$ from Rh(I) and Rh(III). In experiments with $[Rh_2(TFA)_4]$ we found that even under the strongly oxidizing reaction conditions used for the catalytic carbonylation, the robust Rh(II) dimer stays intact and catalytically inactive, for days. A plausible rationale for the beneficial effect of low catalyst concentrations (see Figure 2 and text above) is slower rates of the Rh(I)–Rh (III) dimerization to inactive Rh(II) upon dilution. It is also likely that higher CO pressures slow down the catalytic reaction due to stabilization of Rh(I) and some intermediates of its oxidation to Rh(III).

In conclusion, an unprecedentedly active homogeneous catalytic system has been developed for the direct carboxylation of arenes with exceptionally high chemo- and positional selectivity.

Experimental Section

Synthesis of $[Rh(CO)_2(CF_3CO_2)]_n$[10a]

To a hot solution of $[(acac)Rh(CO)_2]$ (0.50 g) in hexanes (15 mL), TFAH (0.38 mL) was added, in air. Golden crystals of $[Rh(CO)_2(TFA)]_n$ precipitated immediately. After the mixture was kept in an ice bath for 1 hour, the solid product was separated, washed with hexanes, and dried under vacuum; yield: 0.48 g (91%); anal. calcd for $C_4F_3O_4Rh$: C, 17.7; H, 0.0; F, 21.0; found: C, 17.4; H, 0.3; F, 21.0.

Alternatively, $[Rh(CO)_2(CF_3CO_2)]_n$ was prepared by reacting $[Rh(CO)_2Cl]_2$ with AgTFA, or with *t*-BuOK followed by the treatment of the intermediate $[Rh(CO)_2(t\text{-BuO})]_2$ with TFAH.

Oxidation of $[Rh(CO)_2(CF_3CO_2)]_n$

To a stirring suspension of $[Rh(CO)_2(CF_3CO_2)]_n$ (300 mg) in TFAH (7 mL) was added, drop-wise, 30% H_2O_2 (3×0.25 mL). An exothermic reaction occurred instantaneously, and the complex all dissolved. After gas evolution ceased, the solution was refluxed for 5 min, which resulted in a color change from dark-green to bright orange. Another 0.25 mL portion of 30% H_2O_2 was added, after which the solution was refluxed for 30 min and then evaporated to dryness. Drying the residue under vacuum produced an orange amorphous solid (Rh content = 113 mg) which was dissolved in 6.7 mL of TFAH to produce a solution of "$[Rh(TFA)_3]$" with [Rh] = 16. 9 mg/mL.

Carbonylation of Benzene

A mixture of $K_2S_2O_8$ (3.00 g), benzene (5 mL), and TFAH (5 mL) containing "$[Rh(TFA)_3]$" ([Rh] = 4.8×10^{-3} M) was stirred under CO (1 atm) at 25 °C for 48 h. After water (50 mL) was added the mixture was extracted with ether (4×20 mL). The combined ether extracts were dried over $MgSO_4$ and evaporated. Vacuum sublimation of the residue produced 240 mg (TON = 40) of pure PhCOOH (^{1}H NMR and GC-MS).

Carbonylation of Toluene

A mixture of $K_2S_2O_8$ (1.40 g), toluene (5 mL), and TFAH (5 mL) containing "$[Rh(TFA)_3]$" ([Rh] = 3.3×10^{-3} M) was stirred under CO (1 atm) at 50–55 °C for 16 h. GC yield of TolCOOH: TON = 66. Isolated (as described above) yield: 222 mg (TON = 57) of spectroscopically pure TolCOOH (^{1}H NMR: *para*:*meta* = 95 : 5).

Similarly, after 70 h at 25 °C and [Rh] = 1.7×10^{-3} M, TolCOOH (*p*:*m* = 94:6) was obtained with TON = 71.

Carbonylation of Naphthalene (Not optimized)

A mixture of $K_2S_2O_8$ (1.40 g), naphthalene (1 g), and TFAH (5 mL) containing "$[Rh(TFA)_3]$" ([Rh] = 9.7×10^{-3} M) was stirred under CO (1 atm) at 20 °C for 18 h. Isolated yield of 2-naphthoic acid: 52 mg (TON = 6) of >97% isomeric purity (^{1}H NMR, GC-MS). The low TON was likely due to the poor solubility of naphthalene in TFAH. No carboxylation occurred under similar conditions with hexane (5 mL) as a co-solvent.

Carbonylation of Mesitylene (Not optimized)

A mixture of $K_2S_2O_8$ (1.30 g), mesitylene (5 mL), and TFAH (5 mL) containing "$[Rh(TFA)_3]$" ([Rh] = 2.4×10^{-3} M) was stirred under CO (1 atm) at 65 °C for 8 h. Isolated yield of mesitylenecarboxylic acid: 120 mg (TON = 30) of >98% purity (^{1}H NMR, GC-MS).

Carbonylation of *p*-Xylene (Not optimized)

A mixture of $K_2S_2O_8$ (1.40 g), *p*-xylene (5 mL), and TFAH (5 mL) containing "$[Rh(TFA)_3]$" ([Rh] = 4.8×10^{-3} M) was stirred under CO (1 atm) at 20 °C for 24 h. 2,5-Dimethylbenzoic acid was formed with TON = 30 (^{1}H NMR).

References and Notes

[1] For most recent comprehensive reviews, see: (a) A. E. Shilov, G. B. Shul'pin, *Chem. Rev.* **1997**, *97*, 2879; (b) A. E. Shilov, G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers, Dordrecht, **2000**.

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[5] (a) Y. Fujiwara, I. Kawata, H. Sugimoto, H. Taniguchi, *J. Organomet. Chem.* **1983**, *256*, C35; (b) T. Jintoku, Y. Fujiwara, I. Kawata, T. Kawauchi, H. Taniguchi, *J. Organomet. Chem.* **1990**, *385*, 297; (c) R. Ugo, A. Chiesa, *J. Chem. Soc., Perkin Trans. I* **1987**, 2625; (d) Y. Taniguchi, Y. Yamaoka, K. Nakata, K. Takaki, Y. Fujiwara, *Chem. Lett.* **1995**, 345; (e) W. Lu, Y. Yamaoka, Y. Taniguchi, T. Kitamura, K. Takaki, Y. Fujiwara, *J. Organomet. Chem.* **1999**, *580*, 290.

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[9] The homogeneous reaction[8] catalyzed by $[Rh(CO)_2Cl]_2$ (or $[(Ph_3P)_3RhCl]$) and Cu^{2+} was run in mixtures of CF_3COOH and $(CF_3CO)_2O$. High TONs (up to 679) were obtained at 140 °C under ca. 10–17 atm of CO/O_2 in a ratio *within explosive limits*. The Waller method[7] gives lower TONs (2–42) and is safe ($CO/O_2 = 97:3$) but requires high pressures of 130–270 atm at 150 °C.

[10] (a) L. Yu. Ukhin, Yu. A. Shvetsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*. **1972**, 1653; see also: F. J. Lahoz, A. Martin, M. A. Esteruelas, E. Sola, J. L. Serrano, L. A. Oro, *Organometallics*, **1991**, *10*, 1794; (b) Crystal data for $[Rh(CO)_2(CF_3CO_2)]_n$: crystal dimensions $0.12 \times 0.08 \times 0.24$ mm; monoclinic; space group $P2_{1/c}$ (No. 14); $a = 8.165(4)$ Å, $b = 11.821(9)$ Å, $c = 14.756(8)$ Å, $\beta = 94.046(12)°$, $V = 1420.7(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.543$ g cm^{-3} $T = 173$ K; $2\theta_{max} = 48.22°$; Rigaku Raxis-II image plate; of 4439 reflections collected 1788 were unique ($R_{int} = 10.7\%$, $R_{sig} = 7.7\%$); Lorentz and polarization corrections. The structure was solved by direct methods using teXsan^2(SIR-92) and refined (217 parameters) using SHELXTL by full matrix least-squares method on F^2; $R[F^2 > 2\sigma(F^2)] = 0.066$, $wR(F^2$ all data$) = 0.185$ ($w = 1/[\sigma^2(F_o^2) + (0.095P)^2 + 6.865P]$ where $P = (F_o^2 + 2F_c^2)/3$); GOF on $F^2 = 1.10$; data-to-parameter ratio = 8.24; max. residual electron density 0.81 e Å^{-3}. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 145577. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

[11] (a) Upon addition of H_2O_2 to $[Rh(CO)_2(CF_3CO_2)]_n$ in TFAH the originally tan mixture rapidly turns deep-purple, red, green-tan, and then slowly red-orange. Using $[Rh(^{13}CO)_2(CF_3CO_2)]_n$ and monitoring this multistep oxidation by ^{13}C NMR revealed that some of the numerous Rh intermediates are carbonyl complexes. At least 7 different RhCO doublet resonances were observable with δ in the range of 161.0–172.0 ppm with $J_{Rh-C} = 63$ to 72 Hz. A singlet due to $^{13}CO_2$ was observed at 124.8 ppm; (b) We have found that "Rh(III) trifluoroacetate", a mixture of complexes formed by dissolving $Rh_2O_3 \cdot n\,H_2O$ in TFAH,[11c] often contains Cl^- which is detrimental to the C-H activation (see text). The presence of chlorine in the "rhodium oxide hydrate" arises from the common use of $RhCl_3 \cdot n\,H_2O$ to prepare the hydrated oxide. Of 8 different samples of $Rh_2O_3 \cdot n\,H_2O$ used in our work, some obtained commercially and some prepared in our laboratories from $RhCl_3 \cdot n\,H_2O$, all contained chlorine. Importantly, the solubility of "rhodium oxide" appears to change directly with Cl contamination, e. g., the most contaminated sample (10.9% Cl; commercial from Strem) was easily soluble in TFAH, whereas the purest (0.6% Cl; commercial from Strem) did not dissolve in TFAH even upon prolonged heating at 200 °C for 2 days, and eventually decomposed to Rh metal after several hours at 230 °C. Oxidation of $[Rh(CO)_2(CF_3CO_2)]_n$ with H_2O_2 in TFAH affords highly soluble, catalytically active Cl-free Rh(III)-TFA species; (c) N. F. Gol'dshleger, A. P. Moravskii, Yu. M. Shul'ga, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1991**, 258; Yu. M. Shul'ga, N. F. Gol'dshleger, V. I. Rubtsov, V. I. Sokol, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1992**, 1549; N. F. Gol'dshleger, Yu. M. Shul'ga, O. S. Roshchupkina, *Russ. J. Gen. Chem.* **1998**, *68*, 339.

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[13] (a) Trifluoroacetic and other perfluoroalkylcarboxylic acids promote metal-catalyzed activation of alkanes[13b] and arenes;[13c] (b) For reviews, see: A. Sen, *Top. Organomet. Chem.*. **1999**, *3*, 81; *Acc. Chem. Res.*, **1998**, *31*, 550; (c) Very recently, Fujiwara and co-workers reported the Pd- or Pt-catalyzed hydroarylation of alkynes in the presence of TFAH: C. Jia, D. Piao, J. Oyamada, W. Lu, T. Kitamura, Y. Fujiwara, *Science.* **2000**, *287*, 1992; C. Jia, W. Lu, J. Oyamada, T. Kitamura, K. Matsuda, M. Irie, Y. Fujiwara, *J. Am. Chem. Soc.*, **2000**, *122*, 7252.

[14] The addition of chloride ion (PPN Cl) in the amounts of 1, 0.5, and even 0.3 equivalents per Rh shut down H/D exchange between toluene-d_8 and TFAH. When $RhCl_3 \cdot 3\,H_2O$ was used instead of "$Rh(TFA)_3$" for the carbonylation no reaction was observed after one day. However, after 2.5 days, TolCOOH formed with TON = 38. There was no induction period when chloride-free "$Rh(TFA)_3$" was employed, and the long induction period observed when employing $RhCl_3 \cdot 3\,H_2O$ was probably the time needed to oxidize the

chloro ligands with $K_2S_2O_8$/TFAH and produce a sufficiently reactive Rh(III) electrophile.

[15] Determined by running the carbonylation with a 1:1 (molar) mixture of toluene and toluene-d_8, followed by ^{13}C NMR analysis ($D_1 = 30$ sec) of the product.

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[17] Attempts to detect ^{103}Rh NMR signals in a highly concentrated sample of "$Rh(TFA)_3$" (ca. 200 mg Rh in 0.6 mL TFAH) failed. In addition to the intense solvent peak (TFAH, $\delta = -81.0$ ppm) two multiplets at –78.8 and –79.9 ppm (2:1) were observed in the ^{19}F NMR spectrum of this sample at 25 °C, indicating that TFA ligand exchange on the Rh centers is slow on the NMR time scale. While the exact structure of the active Rh(III) electrophile remains unknown, this d^6 species is expected to be octahedral or pentacoordinate and hence possess considerable steric bulk. This would account for the lack of reactivity at the *ortho*-positions of toluene.

[18] Determined by running the carbonylation with a 1:1 (molar) mixture of benzene and toluene, followed by ^1H NMR analysis of the product.

[19] The difference in the *para*-selectivity of the carbonylation (>90%) and H/D exchange (ca. 70%) may be due to slightly different rates of CO insertion into the *m*-Tol-Rh and *p*-Tol-Rh bonds.

[20] While Cu(II) is probably capable of oxidizing Rh(I) under drastic conditions,[8a] no toluene carbonylation occurred in our system (65 °C, 1 atm) when CuX_2 (X = TFA or BF_4) was employed instead of $K_2S_2O_8$.

[21] (a) Although no arene complex formation was observed in solutions of $[(CO)_2Rh(TFA)]_n$ in toluene/TFAH at room temperature under a dinitrogen atmosphere, the addition of $HSbF_6$ or HOTf gave rise to $[(toluene)Rh(CO)_2]^+$ which was converted back to $[(CO)_2Rh(TFA)]_n$ upon addition of CF_3CO_2K. The toluene complex was prepared independently by reacting $[Rh(CO)_2Cl]_2$ with $AgSbF_6$ in CH_2Cl_2/toluene, and isolated as a brown-yellow solid; ^1H NMR (CD_2Cl_2/TFAH): $\delta = 2.6$ (s, 3 H), 7.1 (m, 1 H), 7.15 (m, 4 H); ^{13}C NMR (CD_2Cl_2/TFAH): $\delta = 22.0$ (s, CH_3), 107.0 (d, $J_{Rh-C} = 3$ Hz, *p*-CH), 108.7 (d, $J_{Rh-C} = 3$ Hz, *o*- or *m*-CH), 109.9 (d, $J_{Rh-C} = 3$ Hz, *o*- or *m*-CH), 128.3 (br, *ipso*), 178.1 (d, $J_{Rh-C} = 84$ Hz, CO). The compound undergoes very slow oxidation by H_2O_2 in TFAH at room temperature, possibly via a very small equilibrium concentration of $[(CO)_2Rh(TFA)]_n$. (b) No oxidative carbonylation of toluene took place in the presence of C_6Me_6, probably due to the formation of stable $[(C_6Me_6)Rh(CO)_2]^+$.