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Arylglyoxylrhodium Complexes, Their Thermolysis, and Attempted Generation by Carbonylation of an Aroylrhodium Complex

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Reactions of ArCOCOCl (Ar = *p*-ClC_6H_4, Ph) with Rh(acac)$(CO)_2$ proceeded readily to afford dimeric arylglyoxyl rhodium complexes [Rh(μ-Cl)(acac)(CO)(COCOAr)]$_2$. [Rh(μ-Cl)(acac)(CO)-{COCO(*p*-ClC_6H_4)}]$_2$ was characterized by X-ray diffraction. Thermolysis of the products showed that [Rh(μ-Cl)(acac)(CO){COCO(*p*-ClC_6H_4)}]$_2$ was more stable than [Rh(μ-Cl)(acac)(CO)-(COCOPh)]$_2$. The reaction of *p*-$CH_3OC_6H_4COCOCl$ with Rh(acac)$(CO)_2$ did not form a similar dimeric complex as final product, but gave *p*-$CH_3OC_6H_4COCl$ as major product, showing thermal instability of corresponding arylglyoxyl and aroyl rhodium complexes. The reaction of C_6F_5CO-COCl did not form a simlar dimeric complex either, but a mononuclear complex RhCl(acac)-($COCOC_6F_5$)$(CO)_2$ was generated as a transient intermediate, which was readily transformed to a furanone arising from reductive elimination of the acac ligand and C_6F_5COCO moiety followed by cyclization. In the thermolysis of [Rh(μ-Cl)(acac)(CO)(COCOAr)]$_2$, only ArCOCl and Rh(acac)-$(CO)_2$ were formed, and any ArCORh species could not be detected during the thermolysis process. However, the reaction of Rh(acac)$(CO)_2$ with PhCOCl formed RhCl(acac)$(CO)_2$(COPh), albeit only to a small extent, suggesting that the reaction is not thermodynamically favored. The reaction of RhCl(CO)$(PMe_3)_2$ with *p*-$ClC_6H_4COCOCl$ also proceeded cleanly to furnish *p*-$ClC_6H_4COCORhCl_2$-$(CO)(PMe_3)_2$. Thermolysis of the complex formed *p*-$ClC_6H_4CORhCl_2(CO)(PMe_3)_2$, indicating slow reductive elimination of ClC_6H_4COCl as compared with the ArCORh species, generated in the thermolysis of [Rh(μ-Cl)(acac)(CO)(COCOAr)]$_2$. Treatment of $ClC_6H_4CORhCl_2(CO)(PMe_3)_2$ with carbon monoxide generates *p*-$ClC_6H_4COCORhCl_2(CO)(PMe_3)_2$, although the yield was low.

Introduction

One of us and Yamamoto's group reported palladium-catalyzed carbonylation of aromatic halides forming α-keto acid derivatives in 1982.[1] Although a mechanism involving ArCOCOPd species was one of the options, the possibility was clearly excluded by the facile decarbonylation observed by Sen and co-workers.[2] Since then we have considered tacitly that α-keto acyl complexes are thermodynamically unfavorable, although Sen and co-workers reported that α-keto acyl platinum complexes are more stable than palladium congeners.[3] Palladium-catalyzed carbonylation of imidoyl chlorides, possibly involving somewhat similar α-imino acyl species, has also been reported.[4] Here we wish to disclose that Rh(I) complexes such as Rh(acac)$(CO)_2$[5,6] and RhCl-$(CO)(PMe_3)_2$ react readily with ArCOCOCl to afford significantly stable arylglyoxyl rhodium complexes (ArCOCORh) in high yields. Thermolysis of the products and attempted generation of arylglyoxyl rhodium species by carbonylation of an aroyl rhodium complex are also reported.

Results and Discussion

Reaction of Arylglyoxyl Chlorides with Rh(acac)$(CO)_2$ Forming Di- or Mononuclear Arylglyoxyl Complexes. When a toluene solution of Rh(acac)$(CO)_2$ (**1**) and *p*-ClC_6H_4CO-COCl (**2a**, 2 equiv) was stirred for 6 h at 30 °C, a yellow powder precipitated. Routine workup afforded an analytically pure sample of **3a** in 93% yield (Scheme 1). NMR and IR spectroscopy and elemental analysis were satisfactory, and an X-ray diffraction study verified that **3a** was a

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(1) (a) Ozawa, F.; Soyama, H.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett*. **1982**, *23*, 3383. (b) Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc*. **1985**, *107*, 3235. (c) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem*. **1982**, *233*, C64. (d) Sakakura, T.; Yamashita, H.; Kobayashi, T.; Hayashi, T.; Tanaka, M. *J. Org. Chem*. **1987**, *52*, 5733, and references therein. (e) Kobayashi, T.; Sakakura, T.; Tanaka, M. *Tetrahedron Lett*. **1987**, *28*, 272.

(2) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc*. **1987**, *109*, 148.

(3) For the chemistry of α-keto acyl complexes relevant to double carbonylation and their generation, see: des Abbayes, H.; Salaün, J.-Y. *Dalton Trans*. **2003**, 1041.

(4) Amii, H.; Kishikawa, Y.; Kageyama, K.; Uneyama, K. *J. Org. Chem*. **2000**, *65*, 3404.

(5) Relevant catalysis using this complex will be reported elsewhere.

(6) To the best of our knowledge, there is only one publication reporting oxidative addition of organic halides with Rh(acac)$(CO)_2$. See: Varshavsky, Yu. S.; Cherkasova, T. G.; Struchkov, Yu. T.; Batsanov, A. S.; Bresler, L. S.; Marasanova, N. N. *Koord. Khim*. **1988**, *14*, 1105. *Chem. Abstr*. **1989**, *111*, 39553t.

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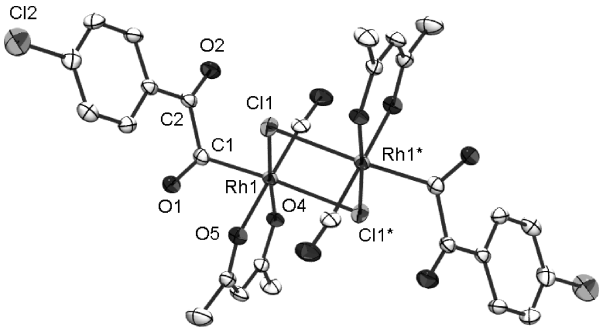
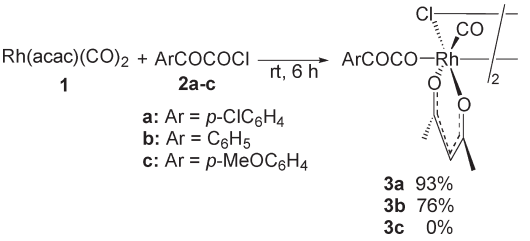


Figure 1. Molecular structure of **3a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity.

Scheme 1



chlorine-bridged dimeric arylglyoxyl complex (Figure 1).[7] Its Rh−C separation in the arylglyoxyl rhodium moiety (1.974 Å) is somewhat short as compared with those of acyl-rhodium complexes, although the deviation from the normal range (2.058−1.992 Å) is not significant[8,9] and agrees with its unexpected thermal stability (mp ∼126 °C).

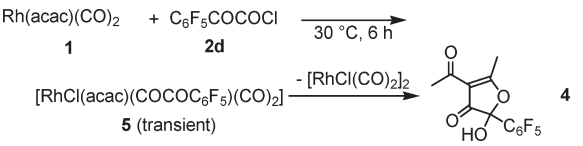
Plain $C_6H_5COCOCl$ (**2b**) also reacted with **1** similarly to afford **3b** in 76% yield. However, *p*-$MeOC_6H_4COCOCl$ (**2c**) displayed totally different reaction behavior under identical conditions. ^{1}H NMR analysis of the resulting mixture indicated that *p*-$MeOC_6H_4COCl$ arising from decarbonylation was the major product (65%), and unreacted **2c** (27%) and **1** (89% based on **1** charged) were also found. Although formation of **3c** could not be confirmed, we can safely presume, in view of decarbonylation and reductive elimination affording *p*-$MeOC_6H_4COCl$ having taken place, that oxidative addition took place to generate **3c** as transient intermediate. Thus, the reactivity of **2c** differs very much from those of **2a** and **2b**, but the reactivity trend agrees with our previous observations that electronegative groups bound to the acyl functionality suppress decarbonylation in rhodium-catalyzed reactions of acyl chlorides.[8a,b,10]

Table 1. Time Course of the Reaction of Rh(acac)$(CO)_2$ with 2d[a]

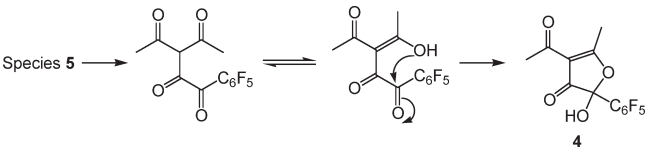
	conversion (%)		yield (%)[b]	
time (h)	**2d**[c]	Rh(acac)$(CO)_2$[b]	**4**	**5**
1	37	39	10	26
2	72	70	55	14
3	100	100	96	3
4	100	100	97	0

[a] Reaction conditions: **2d** (0.053 mmol), Rh(acac)$(CO)_2$ (0.053 mmol), chloroform-*d* (0.5 mL), 30 °C, in an NMR tube. [b] Determined by ^{1}H NMR spectroscopy. [c] Determined by ^{19}F NMR spectroscopy using hexafluorobenzene as an internal standard.

Scheme 2



Scheme 3



The reaction of $C_6F_5COCOCl$ (**2d**) with **1** also formed an arylglyoxyl complex (**5**) as transient species, but the complex was mononuclear and was too labile in another direction to isolate (Scheme 2). A preliminary experiment using **1** and **2d** in a 1:1 ratio at 30 °C for 6 h gave, besides $[RhCl(CO)_2]_2$, compound **4** as the sole product.[11,12] Time course study of the reaction showed complex **5** being formed initially, but later, the quantity of **5** diminished to give **4** at the expense of **5** (Table 1). The formation of **4** can be rationalized as shown in Scheme 3.

The structure of **5** could not be fully characterized due to its lability. However, we are able to safely conclude that compound **5** is a mononuclear arylglyoxyl complex on the bases of (1) NMR spectral features being different from those of **3a** and **3b**, (2) FAB-MS analysis displaying *m*/*z* 481 ($[M - Cl]^+$) unlike **3a** and **3b**, which displayed *m*/*z* 399 and 433, respectively, both corresponding to $[M/2 + H]^+$, (3) final product **4** being formed at the expense of **5**, and (4) $[RhCl(CO)_2]_2$ being nearly the sole rhodium-containing species in the final solution. Somewhat puzzling is that the selective formation of **4** takes place with **2d**, but not with **2a** and **2b**. This may be associated with the high electrophilicity of the C_6F_5COCO group,[13] resulting in the facile C-acylation with the rhodium acetylacetonate, relative to the CO dissociation prerequisite for the formation of **3a** and **3b**.

Thermolysis of [Rh(*μ*-Cl)(acac)(CO)(COCOAr)]$_2$ and Reaction of Rh(acac)$(CO)_2$ with PhCOCl Relevant to the Thermolysis. Although the foregoing experiments have already provided a rough view of the substituent-dependent thermal

(7) An iodine-bridged dimeric acetyl rhodium complex having nearly the same configuration has been reported. See ref 6.

(8) The Rh−C separation is shorter than 2.058−1.992 Å reported for $RhCl_2(CO)(COCH_2Cl)(PMePh_2)_2$, $RhCl_2(CO)(COCH_2Cl)(PMe_3)_2$, $Rh(COC_6F_5)Cl_2(CO)(PMe_3)_2$, and *cis*-$RhCl_2(COPh)(dppp)$, but a little longer than 1.953 Å for *cis*-$Rh(COC_2H_5)CI_2(P(C_6H_5)_3)_2$. See: (a) Kashiwabara, T.; Kataoka, K.; Hua, R.; Shimada, S.; Tanaka, M. *Org. Lett.* **2005**, *7*, 2241. (b) Kashiwabara, T.; Fuse, K.; Hua, R.; Tanaka, M. *Org. Lett.* **2008**, *10*, 5469. (c) McGuiggan, M. F.; Doughty, D. H.; Pignolet, L. H. *J. Organomet. Chem.* **1980**, *185*, 241. (d) Shie, J.-Y.; Lin, Y.-C.; Wang, Y. *J. Organomet. Chem.* **1989**, *371*, 383.

(9) A very short Rh−C separation (1.85 Å) was noted for $Rh(COCH_2CH_2Ph)CI_2(P(C_6H_5)_3)_2$ in a trigonal-bipyramidal arrangement in which the two phosphines were in apical positions. However this value came from a preliminary X-ray structure determination, which was stopped at $R = 0.20$ stage of the refinement. The final value does not appear to have been published. See: Lau, K. S. Y.; Becker, Y.; Huang, F.; Baenziger, N.; Stille, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 5664.

(10) (a) Hua, R.; Shimada, S.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 12365. (b) Hua, R.; Onozawa, S.-y.; Tanaka, M. *Chem. Eur. J.* **2005**, *11*, 3621.

(11) Nonhebel, D. C.; Smith, J. *J. Chem. Soc.* (*C*) **1967**, 1919.

(12) The structure was confirmed by X-ray analysis. See the Supporting Information.

(13) Kivinen, A. In *The Chemistry of Acyl Halides*; Patai, S., Ed.; Interscience Publishers: London, 1972; Chapter 6.

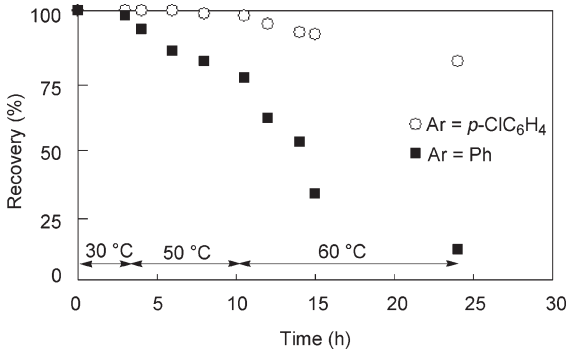


Figure 2. Time course of the thermolysis of complexes **3a** and **3b**. Thermolysis temperature: 30 °C (0−3 h), 50 °C (3−10.5 h), 60 °C (10.5−24 h).

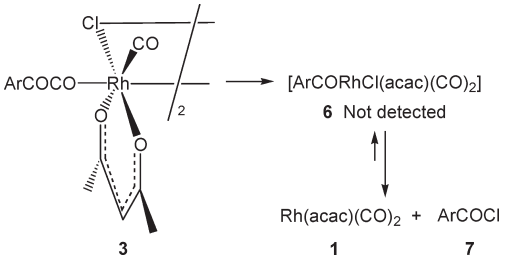
stability of arylglyoxyl rhodium complexes, high stability of **3a** as compared with **3b** is more distinctly seen in the thermolysis of these complexes. A benzene-d_6 solution of **3a** or **3b** was heated in an NMR tube under nitrogen at 30 °C for 3 h, then at 50 °C for an additional 7.5 h, and finally at 60 °C for an additional 13.5 h. The thermolysis proceeded cleanly to form only $Rh(acac)(CO)_2$ and corresponding ArCOCl. In the thermolysis of **3a**, 81% of **3a** still remained unchanged even after these three-step processes (Figure 2). Complex **3b** also survived after the second process at 50 °C, albeit in a less significant quantity (75%), clearly suggesting that the benzoyl group in the phenylglyoxyl group is electronegative enough to stabilize **3b**. However, since **3b** did not have an extra electronegative group like chlorine in **3a**, it underwent decarbonylation more rapidly upon heating at 60 °C. The rate constants of the thermolysis of **3a** and **3b** at 60 °C were 4.2×10^{-11} and 3.0×10^{-10} mol/s, respectively.

What is interesting in the thermolysis study is that ^{1}H NMR spectroscopy showed basically only the signals of complex **3**, aroyl chloride **7**, and **1**; any other species such as corresponding aroyl rhodium complex **6** was not detected in an appreciable quantity. This indicates that the thermal decomposition proceeds as shown in Scheme 4 and that **6**, a possible intermediate, is far more labile toward reductive elimination than **3**.

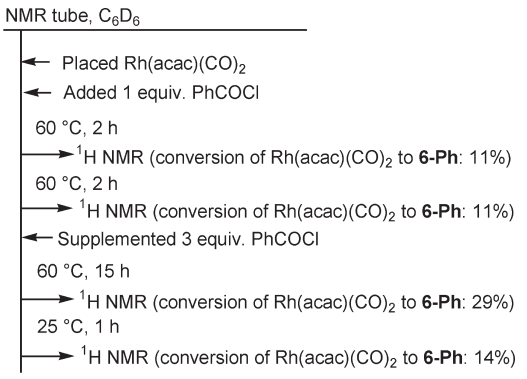
Despite the foregoing statement, careful analysis of a 1:1 mixture of complex **1** and benzoyl chloride in benzene-d_6 left standing at room temperature for 1 h did show new species (**6-Ph**), but the yield was only 3%. The yield did not change over a period of an additional 2 h, indicating that the extent of the reaction was thermodynamically controlled under the conditions. The equilibrium constant under the conditions is evaluated at 1.52×10^3 mol^{-1}. Following this, benzoyl chloride (2 equiv) was supplemented to the mixture and the reaction was continued further for another 2 h to boost the yield to 12%. Another sequence of similar operations carried out at 60 °C also provided similar results (Scheme 5), but the yield of **6-Ph** was generally higher.[14] The equilibrium constant on the basis of the conversion after the initial 2 h is evaluated at 7.28×10^3 mol^{-1}. Although species **6** was formed to a minor extent under these conditions, the observations also conclude that the oxidative addition of **7** with **1**, unlike the reaction of **2** with **1**, is not a thermodynamically favored process and that a majority of species **6** possibly generated in the thermolysis of **3** reductively eliminates **7** readily.

(14) As Scheme 5 indicates, upon cooling the mixture to room temperature after the sequential treatment at 60 °C, the yield decreased.

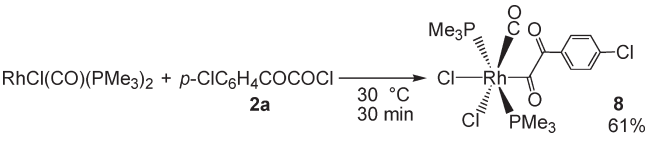
Scheme 4



Scheme 5



Scheme 6

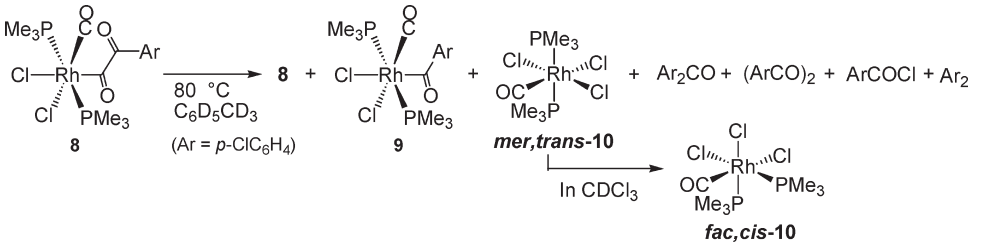


Formation of p-$ClC_6H_4COCORhCl_2(CO)(PMe_3)_2$ by the Reaction of p-Chlorophenylglyoxyl Chlorides with $RhCl(CO)(PMe_3)_2$ and Its Thermolysis. Finally, we took a brief look at the reaction of $RhCl(CO)(PMe_3)_2$ with **2a** (1 equiv) at 30 °C, which did furnish corresponding arylglyoxyl complex **8** in 61% yield (Scheme 6). We were unable to obtain a crystal suitable for X-ray analysis. However, characterization by NMR and IR spectroscopy combined with our previous observations[8a,b,10] supports that the structure is that illustrated in Scheme 6.

Thermolysis of complex **8** has revealed that the complex is also fairly stable, in particular under carbon monoxide. Unlike the lack of observable formation of **6** (Scheme 4) in the thermolysis of **3a** and **3b**, thermolysis of **8** at 80 °C leads to the formation of fairly stable p-chlorobenzoylrhodium complex **9** besides other products arising from **8** and/or **9** (Table 2). The higher stability of **9** as compared with possible intermediate **6** is associated with the trimethylphosphine ligated to the rhodium center.

In practice of the thermolysis, a toluene-d_8 solution of **8** in an NMR tube was heated at 80 °C for 1 h under nitrogen. Only 12% of **8** remained and **9** was found in 56% yield, as analyzed by ^{1}H NMR spectroscopy. After heating at 80 °C for an additional 1 h, analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy confirmed that **8** did not remain in the final solution and that, in addition to **9** (47%, which was quantified by ^{1}H NMR spectroscopy), *mer,trans*-$RhCl_3(CO)(PMe_3)_2$ (***mer,trans*-10**) was also formed. More detailed analysis by ^{1}H NMR spectroscopy (with p-dimethoxybenzene

Table 2. Thermolysis of *p*-$ClC_6H_4COCORhCl_2(CO)(PMe_3)_2$ (8) at 80 °C



other conditions[a]	recovery of **8** (%)[b]	yield (%)[b], Ar = *p*-ClC_6H_4					
		9	***fac*,*cis*-10**	Ar_2CO	$(ArCO)_2$	ArCOCl	Ar_2
1 h, N_2	12	56					
2 h, N_2	0	47	22	0	20	8	trace
1 h, CO 80 atm	> 72[c]	< 20[c]	3	3	6	0	trace

[a] Other conditions: 80 °C, toluene-d_8 solvent. [b] Recovery of **8** and formation of **9** and ***mer*,*trans*-10** were confirmed by ^{31}P NMR spectroscopy of the reaction mixture (toluene-d_8 solution) by using authentic samples. Note that ***mer*,*trans*-10**, which was detected in the toluene-d_8 solution, isomerized to ***fac*,*cis*-10** upon replacement of the solvent with $CDCl_3$ due to the solvent-dependent isomerization. Recovery of **8** and the yields of the products listed were determined by ^1H NMR spectroscopy in $CDCl_3$ after evaporation of toluene-d_8 and dissolving the residue in $CDCl_3$. Yields of Ar_2CO, $(ArCO)_2$, ArCOCl, and Ar_2 are referenced to the quantity of Ar group. [c] See ref 16.

as internal standard) using a $CDCl_3$ solution of a residue obtained by evaporation of the final mixture in toluene-d_8 revealed the formation of dichlorobenzil, *p*-chlorobenzoyl chloride, and dichlorobiphenyl. Dichlorobenzophenone was not found at all. *mer,trans*-$RhCl_3(CO)(PMe_3)_2$ (***mer*,*trans*-10**), which was detected before the replacement of the solvent from toluene-d_8 to $CDCl_3$, was not found either, but instead, *fac*,*cis*-$RhCl_3(CO)(PMe_3)_2$ (***fac*,*cis*-10**) was found in the $CDCl_3$ solution. In view of facile isomerization between ***mer*,*trans*-10** and ***fac*,*cis*-10**, depending on the polarity of the solvent,[15] ***mer*,*trans*-10** found in the thermolysis mixture (*a toluene-d_8 solution*) appeared to have isomerized to ***fac*,*cis*-10** when the toluene-d_8 solvent was replaced by $CDCl_3$.

On the other hand, upon thermolysis under CO (80 atm) at 80 °C for 1 h, > 72% of **8** survived and **9** was formed only in < 20%.[16] Other products were also formed as summarized in Table 2.

Attempts to Generate *p*-$ClC_6H_4COCORhCl_2(CO)(PMe_3)_2$ by Carbonylation of *p*-$ClC_6H_4CORhCl_2(CO)(PMe_3)_2$. Worth noting, associated with the foregoing formation and the stability of **8**, is that treatment of *p*-$ClC_6H_4CORhCl_2(CO)(PMe_3)_2$ (**9**) with carbon monoxide generates species **8** in situ (Scheme 5), albeit in a low yield due to side reactions of **9**. When a solution of **9** in $CDCl_3$ was heated at 40 °C under carbon monoxide (80 atm) for 6 h, only decomposition of **9** appeared to have taken place to give dichlorobenzophenone, dichlorobenzil, *p*-chlorobenzoyl chloride, and others, besides unreacted **9** (18%) and *fac*,*cis*-$RhCl_3(CO)(PMe_3)_2$ (**10**, 46%) as major rhodium-containing species (Table 3, Figure 3).[17] However, another reaction run at 80 °C in toluene-d_8 for 6 h resulted in emergence of ^{31}P NMR signals characteristic of **8** (−3.44 ppm, d, J_{P-Rh} = 84.1 Hz in $CDCl_3$). Its yield was estimated at 4% by ^1H NMR spectroscopy, and other products from **8** and/or **9** were also formed. Although the yield of **8** is low, this observation is encouraging in view of application to rhodium-catalyzed reactions of aroyl chlorides under CO pressure to afford arylglyoxylated products.[5]

To summarize, arylglyoxyl rhodium complexes can be readily synthesized by oxidative addition of arylglyoxyl chloride. Unlike α-keto acyl palladium complexes, they are fairly stable as opposed to our tacit understanding and can be generated by CO insertion reaction with aroyl rhodium complexes. Catalysis involving them as key intermediates will be reported shortly.

Experimental Section

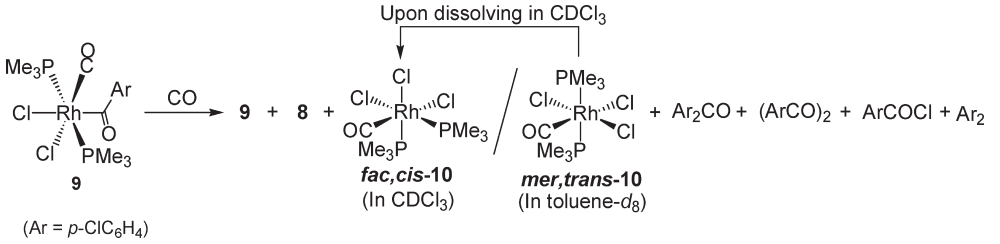
[Rh(μ-Cl)(acac)(CO)($COCOC_6H_4$-*p*-Cl)]$_2$ (3a). To a yellow solution of Rh(acac)$(CO)_2$ (97.1 mg, 0.376 mmol) in toluene (5 mL) placed in a 20 mL Schlenk tube was added *p*-ClC_6H_4CO-COCl (151.8 mg, 0.752 mmol) at 30 °C, and the mixture was stirred for 6 h at the temperature. While the reaction was in progress, yellow powders precipitated. Volatiles were removed in vacuo to give a yellow material, which was rinsed with ether (1 mL) and hexane (3 mL × 3) and was dried in vacuo to afford analytically pure **3a** (153.0 mg, 0.176 mmol, 93%): yellow needles: mp 125.8−126.3 °C (under nitrogen). ^1H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 8.58 Hz, 2H, *m*-Ph), 7.44 (d, J = 8.58 Hz, 2H, *o*-Ph), 5.62 (s, 1H, acac-CH), 2.19 (s, 3H, Me), 1.97 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 209.8 (br, Rh-CO), 186.9 (acac-CO), 186.7 (Ar*C*OCORh), 181.4 (acac-CO), 176.9 (d, $^1J_{Rh-C}$ = 66.8 Hz, Rh-*C*OCO), 141.6 (*p*-Ph), 131.5 (*o*-Ph), 129.4 (*m*-Ph), 128.0 (*ipso*-Ph), 100.5 (CH), 26.9 (Me), 26.4 (Me). IR (KBr, cm^{-1}): 2106 (Rh-CO), 1736, 1678 (RhCOCOAr), 1558,

(15) (a) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061. (b) Kashiwabara, T.; Fuse, K.; Muramatsu, T.; Tanaka, M. *J. Org. Chem.* **2009**, *74*, 9433.

(16) To evaluate the conversion from **8** to **9**, we have to take into account the fact that the conversion is much faster under nitrogen than that under CO. In the thermolysis under CO, CO was introduced *approximately 3 min after the toluene-d_8 solution of complex **8** had been charged to the autoclave preheated at 80 °C*. Then the mixture was stirred for 1 h at 80 °C. In view of the foregoing thermolysis effected in the absence of carbon monoxide, thermal decomposition of **8** is envisioned to have taken place, during this 3 min time lag under nitrogen atmosphere, to a small extent (∼5% conversion of **8**; see Table S1 for detailed conversion data obtained in the thermolysis under nitrogen to estimate this conversion during the 3 min time lag). If we deduct the conversion of **8** made before introduction of CO, the net conversion of **8** after CO introduction can be estimated at ∼23% (recovery of **8**: ∼77%) and the quantity of **9** formed at ∼17%. The same argument can be made for the quantity of other products listed in Table 2.

(17) We are unable to rigorously exclude the possibility that the species displaying a doublet at −7.11 ppm (J_{P-Rh} = 117.2 Hz) in the ^{31}P NMR spectrum (Figure 3, the second spectrum from the bottom) is an intermediate toward the formation of **8**.

Table 3. Reaction of *p*-ClC$_6$H$_4$CORhCl$_2$(CO)(PMe$_3$)$_2$ (9) with Carbon Monoxide



conditions[a]	recovery of **9** (%)[b]	yield (%)[b], Ar = *p*-ClC$_6$H$_4$					
		8	***fac,cis*-10**	Ar_2CO	$(ArCO)_2$	ArCOCl	Ar_2
$CDCl_3$, 40 °C	18	0	46	15	20	21	0
toluene-d_8, 80 °C	0	4	61	33	10	0	5

[a] Other conditions: CO 80 atm, 6 h. [b] Refer to footnote *b* of Table 2.

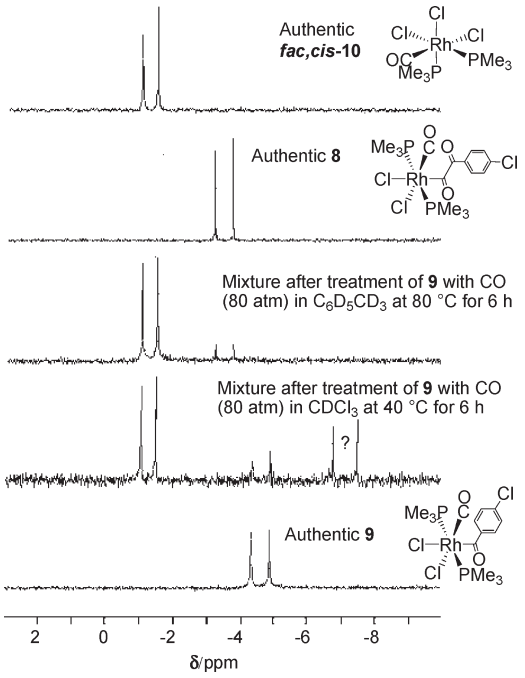


Figure 3. ^{31}P NMR spectra of final mixtures of carbonylation of complex **9** (after replacement of the solvent with $CDCl_3$ in the case of the reaction run in toluene-d_8) with reference complexes.

1519 (acac-C=O). MS (FAB, matrix = 3-nitrobenzyl alcohol): *m*/*z* 433 ([M/2 + H]$^+$). Anal. Calcd for $C_{28}H_{22}Cl_4O_{10}Rh_2$: C, 38.83; H, 2.56. Found: C, 38.44; H, 2.92.

[Rh(*μ*-Cl)(acac)(CO)(COCOC$_6$H$_5$)]$_2$ (3b). To a yellow solution of Rh(acac)(CO)$_2$ (74.5 mg, 0.289 mmol) in toluene (3 mL) placed in a 20 mL Schlenk tube was added PhCOCOCl (50.0 mg, 0.296 mmol) at room temperature, and the mixture was stirred for 6 h at that temperature. Volatiles were removed in vacuo. A yellow oil obtained was rinsed with ether (1 mL × 2) and hexane (1 mL×2) to generate a yellow powder, which was dried in vacuo to afford **3b** (87.1 mg, 0.11 mmol, 76%): yellow crystals, mp 72.3−73.9 °C (under nitrogen, dec). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.84 (d, *J* = 8.13 Hz, 2H, Ph), 7.59 (t, *J* = 7.59 Hz, 1H, *p*-Ph), 7.46 (m, 2H, Ph), 5.48 (s, 1H, acac-CH), 2.17 (s, 3H, acac-Me), 1.85 (s, 3H, acac-Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): *δ* 210.2 (d, $^1J_{Rh-C}$ = 29.0 Hz, Rh-CO), 187.1 (acac-CO), 186.6 (Ph*C*OCORh), 182.4 (acac-CO), 177.3 (d, $^1J_{Rh-C}$ = 66.9 Hz, PhCO*C*ORh), 134.8 (*p*-Ph), 130.4 (*o*-Ph), 129.0 (*ipso*-Ph), 128.2 (*m*-Ph), 100.5 (CH), 26.3 (Me), 25.7 (Me). IR (KBr, cm^{-1}): 2108 (Rh-CO), 1725, 1675 (RhCOCOPh), 1560, 1522 (acac-CO). MS (FAB, matrix = 3-nitrobenzyl alcohol): *m*/*z* 399 ([M/2 + H]$^+$). HRMS (FAB, matrix = 3-nitrobenzyl alcohol): calcd for $C_{14}H_{12}ClO_5Rh$ ([M/2 + H]$^+$) *m*/*z* 398.9507, found 398.9510. Anal. Calcd for $C_{28}H_{24}Cl_2O_{10}Rh_2$: C, 42.19; H, 3.03. Found: C, 41.44; H, 3.35. For NMR spectra of this compound, see Appendices 1 and 2 in the Supporting Information.

Attempted Synthesis of [Rh(*μ*-Cl)(acac)(CO)(COCOC$_6$H$_4$-*p*-OMe)]$_2$ (3c) by the Reaction of Rh(acac)(CO)$_2$ with *p*-MeOC$_6$H$_4$COCOCl (2c). To a yellow solution of Rh(acac)(CO)$_2$ (8.2 mg, 0.0318 mmol) in C_6D_6 (0.4 mL) placed in an NMR tube was added *p*-MeOC$_6$H$_4$COCOCl (9.0 mg, 0.0454 mmol) at room temperature, and the mixture was stirred for 6 h at 30 °C. ^{1}H NMR analysis of the final mixture using intentionally added silicone grease as an internal standard revealed that *p*-MeOC$_6$H$_4$COCl (65% relative to the quantity of **2c** charged), unreacted **2c** (27%), and **1** (89% based on **1** charged) were present. No signal assignable to **3c** was observed.

Reaction of Rh(acac)(CO)$_2$ with C$_6$F$_5$COCOCl (2d) Affording 4. To a yellow solution of Rh(acac)(CO)$_2$ (30.2 mg, 0.233 mmol) in toluene (5 mL) placed in a 20 mL Schlenk tube was added $C_6F_5COCOCl$ (60.3 mg, 0.0233 mmol) at room temperature, and the mixture was stirred for 6 h at 30 °C. Volatiles were removed in vacuo. A ocher solid material obtained was rinsed with hexane (3 mL × 3) and ether (1 mL × 2) and was dried in vacuo to afford analytically pure **4** (56.3 mg, 0.174 mmol, 75%).

4-Acetyl-2-hydroxy-5-methyl-2-pentafluorophenyl-3-furanone (4): pale yellow solid, mp 152.9−153.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 5.39 (br, 1H, OH), 2.69 (s, 3H, Me), 2.48 (s, 3H, Me). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): *δ* 196.8 (CH_3CO), 193.6 (d, J_{CF} = 30.4 Hz, C_6F_5CCO), 147.4−136.3 (m, Ar^F), 112.8 ($C_6F_5COCCH_3$), 109.4 (t, J_{CF} = 10.8 Hz, COH), 100.6 (Ac*C*), 29.9 (*C*H$_3$CO), 18.4 ($C_6F_5COCCH_3$). ^{19}F NMR (282 MHz, $CDCl_3$): *δ* −139.1 (m, 2F, *o*-Ph), −150.1 (m, 1H, *p*-Ph), −160.2 (m, 2F, *m*-Ph). IR (KBr, cm^{-1}): 3102 (br, ν_{OH}), 1731 (ν_{CO}), 1657 (ν_{CO}), 1550 ($\nu_{C=C}$). MS (FAB, matrix = 3-nitrobenzyl alcohol): *m*/*z* 323 ([M + H]$^+$). Anal. Calcd for $C_{13}H_7F_5O_4$: C, 48.46; H, 2.19. Found: C, 48.10; H, 2.28.

Time-Course Study of the Reaction of Rh(acac)(CO)$_2$ with C$_6$F$_5$COCOCl (2d). To a yellow solution of Rh(acac)(CO)$_2$ (13.7 mg, 0.0531 mmol) in $CDCl_3$ (0.5 mL; a small quantity of silicone grease was intentionally added as an internal standard for ^{1}H NMR spectroscopy) placed in an NMR tube were added $C_6F_5COCOCl$ (13.8 mg, 0.0531 mmol) and C_6F_6 (2.0 *μ*L; internal standard for ^{19}F NMR spectroscopy) at room temperature, and ^{1}H and ^{19}F NMR spectra were recorded. Then the mixture was stirred for 4 h at 30 °C. The progress of the reaction was monitored by ^{1}H and ^{19}F NMR analysis every 1 h (Table 1).

FAB-MS analysis using a 1 *μ*L portion taken from the reaction mixture was also performed after stirring for 2 h to

gain information of mononuclear α-keto acyl complex **5**. Also, after 4 h, the IR spectrum was recorded to show ν_{CO} bands at 2104, 2085, 2036, and 2002 cm^{-1}, which agreed with literature data for $[RhCl(CO)_2]_2$.[18] Finally, $PMePh_2$ (26.3 mg, 0.1314 mmol) was added to the mixture; bubbles coming out from the mixture could be confirmed by sight, and $RhCl(CO)(PMePh_2)_2$ having been formed was also confirmed by ^1H and ^{31}P NMR spectroscopy (89% as quantified by ^1H NMR spectroscopy).

RhCl(acac)($COCOC_6F_5$)$(CO)_2$ (5). This compound is a transient species found during the foregoing time-course study. Collection of full characterization data was hampered by the lability. However, its identity is well supported as discussed in the foregoing section. ^1H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 6H, Me), 5.51 (s, 1H, acac-CH). ^{19}F NMR (282 MHz, $CDCl_3$): δ −136.2 (m, 2F, *o*-Ph), −144.1 (m, 1F, *p*-Ph), −159.6 (m, 2F, *m*-Ph). MS (FAB, matrix = 3-nitrobenzyl alcohol): *m*/*z* 481 ($[M - Cl]^+$).

Time-Course Study on Thermolysis of [Rh(μ-Cl)(acac)(CO)($COCOC_6H_4X$)]$_2$ (3a; X = Cl, 3b; X = H). Complex **3a** (6.6 mg) or **3b** (8.54 mg) was dissolved in C_6D_6 (0.5 mL, a small quantity of silicone grease was added intentionally as internal standard for NMR spectroscopy), and the solution was heated at 30 °C for 3 h, then at 50 °C for an additional 7.5 h, and finally at 60 °C for a final 13.5 h (altogether 24 h). The progress of the thermolysis was monitored by ^1H NMR spectroscopy. The progress is illustrated in Figure 2.

RhCl(acac)$(CO)_2$(COPh) (6-Ph). This compound could not be isolated due to instability, but the compound in the mixture of the reaction of Rh(acac)$(CO)_2$ (**1**) with PhCOCl (**7-Ph**) in benzene-d_6 could be characterized. ^1H NMR (300 MHz, C_6D_6): δ 7.93 (m, 2H, *o*-Ph), 7.08 (t, *J* = 7.38 Hz, *p*-Ph), 4.93 (s, 1H, CH), 1.58 (s, 6H, Me). The signal of *m*-Ph overlapped with free PhCOCl. IR (benzene-d_6 solution, cm^{-1}): 2088, 2032 (Rh-CO), 1731 (Rh-COPh), 1205, 1174 (acac-CO). HRMS (FAB, matrix = 3-nitrobenzyl alcohol): calcd for $C_{14}H_{13}ClO_5Rh$ ($[M + H]^+$) *m*/*z* 398.9507, found 398.9519.

$RhCl_2$(CO)($COCOC_6H_4Cl$)$(PMe_3)_2$ (8). To a yellow solution of $RhCl(CO)(PMe_3)_2$ (97.0 mg, 0.305 mmol) in toluene (5 mL) placed in a 20 mL Schlenk tube was added *p*-$ClC_6H_4COCOCl$ (61.9 mg, 0.305 mmol) at room temperature. The color of the mixture changed to reddish-yellow instantaneously. The mixture was stirred at 30 °C for 30 min and was evaporated. The orange solid residue was rinsed with ether (2 mL × 2) and hexane (3 mL × 2) and was dried in vacuo to afford **8** (97.14 mg, 0.186 mmol, 61%): pale yellow powder, mp 112.0−113.3 °C (under nitrogen). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, *J* = 8.39 Hz, 2H, *o*-Ph), 7.46 (d, *J* = 8.39 Hz, 2H, *m*-Ph), 1.70 (virtual t, *J* = 4.00 Hz, 18 H, PMe_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 223.8 (dt, J_{C-P} = 5.81 Hz, J_{C-Rh} = 30.52 Hz, Rh-CO), 186.7 (dt, J_{C-P} = 2.18 Hz, J_{C-Rh} = 4.36 Hz, RhCOCO), 182.7 (dt, J_{C-P} = 10.17 Hz, J_{C-Rh} = 66.85 Hz, Rh*C*OCO), 141.6 (*p*-Ph), 131.4 (*o*-Ph), 129.3 (*m*-Ph), 128.5 (*ipso*-Ph), 14.22 (virtual t, J_{C-P} = 18.17 Hz, PMe_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −3.44 (d, J_{P-Rh} = 84.08 Hz). IR (KBr, cm^{-1}): 2072 (Rh-CO), 1714, 1668 (br, Rh-COCOAr). HRMS (FAB, matrix = 3-nitrobenzyl alcohol): calcd for $C_{15}H_{22}Cl_2O_3P_2Rh$ ($[M - Cl]^+$) *m*/*z* 484.9476, found 484.9467. For NMR spectra of this compound, see Appendices 3−5 in the Supporting Information.

$RhCl_2$(CO)(COC_6H_4Cl)$(PMe_3)_2$ (9). To a yellow solution of $RhCl(CO)(PMe_3)_2$ (100.1 mg, 0.314 mmol) in toluene (5 mL) placed in a 20 mL Schlenk tube was added *p*-ClC_6H_4COCl (40.0 μL, 0.315 mmol) at room temperature. The mixture was stirred at 30 °C for 3 h, while the color changed gradually to slightly dark yellow. The resulting mixture was evaporated. The yellow solid residue was rinsed with ether (2 mL × 2) and hexane (3 mL × 2) and was dried in vacuo to afford analytically pure **9** (136.2 mg, 0.276 mmol, 88%): pale yellow powder, mp 100.2−102.8 °C (under nitrogen, dec). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.06 (d, *J* = 8.79 Hz, 2H, *o*-Ph), 7.50 (d, *J* = 8.79 Hz, 2H, *m*-Ph), 1.71 (virtual t, *J* = 3.60 Hz, 18H, PMe_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 132.4, 130.1, 128.2, 129.4, 14.6 (virtual t, J_{PC} = 16.7 Hz, Me). Signals associated with carbons in the carbonyl groups were too weak to be observable due presumably to multiple coupling with P and Rh nuclei. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −4.63 (d, J_{P-Rh} = 86.02 Hz). IR (KBr, cm^{-1}): 2083 (RhCO), 1675 (RhCOAr). MS (FAB, matrix = 3-nitrobenzyl alcohol): *m*/*z* 457 ($[M - Cl]^+$). Anal. Calcd for $C_{14}H_{22}Cl_3O_2P_2Rh$: C, 34.04; H, 4.49. Found: C, 33.90, H, 4.13.

Treatment of $RhCl_2$(CO)(COC_6H_4Cl)$(PMe_3)_2$ with CO (80 atm) at 80 °C in Toluene-d_8. To $RhCl(CO)(PMe_3)_2$ (18.3 mg, 0.0370 mmol) placed in a 20 mL Schlenk tube were added silicone grease (2.9 mg; internal standard for ^1H NMR analysis) and toluene-d_8 (2.0 mL). The solution was transferred to a 20 mL autoclave (fitted with a glass insert). Carbon monoxide was introduced at 80 atm, and the autoclave was heated at 80 °C for 6 h. Carbon monoxide was vented, and the yellow solution taken out from the autoclave was transferred to a Schlenk tube and evaporated. *p*-Dimethoxybenzene (5.8 mg) as internal standard for NMR spectroscopy and $CDCl_3$ were added, and the resulting solution was analyzed by NMR spectroscopy.

^1H and ^{31}P NMR analysis revealed that rhodium-containing species, **8** and *fac,cis*-$RhCl_3(CO)(PMe_3)_2$ (***fac,cis*-10**), were in this $CDCl_3$ solution together with other organic compounds shown in Table 3. Starting rhodium complex **9** did not remain at all. The ^{31}P NMR spectrum of this $CDCl_3$ solution and that of a similar reaction run at 40 °C for 6 h are shown in Figure 3, which includes relevant species for comparison.

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Supporting Information Available: Experimental details and characterization of new compounds, NMR spectra of **3b** and **8**, which did not furnish satisfactory elemental analysis, and crystallographic data for **3a** and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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