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Palladium-Catalyzed Formation of Aroylcobalt Complexes from Iodoarenes and Tetracarbonylcobaltate(-1) Anion and Syntheses of the Model Intermediate Complexes

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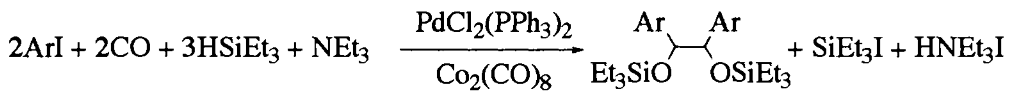
Anion complex $[Co(CO)_4]^-$ reacted with iodoarenes to form aroylcobalt complexes in the presence of a palladium catalyst and excess PPh_3. As models of the intemediate of this reaction, Pt-Co and Pd-Co dinuclear complexes were synthesized from reactions of $[Co(CO)_4]^-$ with $Pt(Ar)(OTf)(PPh_3)_2$ and $Pd(Ar)(OTf)(PMe_3)_2$, respectively, and their crystal structures were determined by X-ray analysis.

Homogeneous bimetallic and multimetallic systems have attracted increasing attention due to their unique catalytic activities arising from synergistic effects of individual metals.[1)] We have been engaged in developing novel bimetallic catalysis, and reported carbonylation reactions using Co-Ru[2)] and Pd-Ru[3)] bimetallic catalysts. More recently we have found that the $PdCl_2(PPh_3)_2$-$Co_2(CO)_8$ system is effective for carbonylation of iodoarenes with hydrosilanes giving 1,2-diaryl-1,2-disiloxyethane in the presence of triethylamine (Eq. 1), although neither $PdCl_2(PPh_3)_2$ nor $Co_2(CO)_8$ shows the catalytic activity by itself.[4)]



$$2ArI + 2CO + 3HSiEt_3 + NEt_3 \xrightarrow[Co_2(CO)_8]{PdCl_2(PPh_3)_2} \underset{Et_3SiO}{\overset{Ar}{\rangle}}\!\!-\!\!\underset{OSiEt_3}{\overset{Ar}{\langle}} + SiEt_3I + HNEt_3I \quad (1)$$

With regard to the mechanism of the reaction (Eq. 1), we presume that the first step is oxidative addition of ArI to the Pd(0) species, which is followed by migration of the aryl or aroyl group from the palladium to cobalt. Since the catalytic arylation of anionic complexes such as $[CpMo(CO)_3]^-$, $[Mn(CO)_5]^-$, and $[CpFe(CO)_2]^-$ by haloarenes with palladium or nickel catalysts have recently been reported,[5)] we have investigated the Pd-catalyzed arylation of $[Co(CO)_4]^-$, which is a plausible active species in the reaction of Eq. 1.

It is known that $[Co(CO)_4]^-$ reacts with haloalkanes or acid halides to give alkyl or acylcobalt complex, respectively,[6)] but not with haloarenes under analogous conditions. We have found that a palladium catalyst effectively promotes the reaction of $[Co(CO)_4]^-$ with ArI and PPh_3 to form $ArCOCo(CO)_3(PPh_3)$ (Eq. 2). Thus, when iodoarene (0.5 mmol) was added to a THF solution of $K[Co(CO)_4]$ (0.75 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and PPh_3 (0.55 mmol) at 50 °C in the dark, KI (identified by EPMA) precipitated gradually and consumption of the iodoarene was disclosed by the GLC analysis. From the reaction mixture, a yellow crystalline solid was isolated by using column chromatography and identified to be an aroylcobalt complex $ArCOCo(CO)_3(PPh_3)$ by IR and ^1H NMR.

$$\mathbf{ArI + K[Co(CO)_4] + PPh_3 \xrightarrow[Pd(PPh_3)_4]{} ArCOCo(CO)_3(PPh_3) + KI} \qquad \mathbf{(2)}$$

Table 1. Formation of Aroylcobalt Complexes Catalyzed by Palladium Complex

Ar	Reaction time/h	Conversion/%[a]	Yield/%[b]
Ph	4	98	73
p-Tol	4	100	79
o-Tol	6	75	32
p-ClC_6H_4	4	98	68
p-$MeOC_6H_4$	4	100	81

a) Based on the starting ArI and determined by GLC analysis. b) Isolated yield.

The results with several iodoarenes are tabulated in Table 1. In the case of iodobenzene and *p*-substituted iodobenzenes, the conversion reached almost 100% within 3–4 h, and the yields of the aroylcobalt complexes were fairly high. However, the reaction of *o*-TolI was much slower and the yield was only 32% after 6 h.

The above reaction was supposed to proceed via the initial oxidative addition of the ArI to a Pd(0) center and the following ligand migration of the aryl (or aroyl) group to $[Co(CO)_4]^-$ anion. Komiya et al. have reported that a series of dinuclear complexes $(COD)RPt-MCp(CO)_3$ (R=alkyl or aryl; M=Mo, W) undergo the migration of the R group to give $RMCp(CO)_3$ through the formal reductive elimination from the Pt center.[7] A Pd–Co dinuclear complex is therefore considered to be an intermediate for the present catalytic reaction (Eq. 2), and we have tried to prepare some model complexes for such a dinuclear intermediate.

Attempts to obtain a Pd–Co bimetallic complex with PPh_3 ligands have been unsuccessful. Indeed, in the reaction of *p*-$TolPdI(PPh_3)_2$ and $K[Co(CO)_4]$, the only species identified from the IR spectra of the reaction mixture was *p*-$TolCOCo(CO)_3(PPh_3)$ probably due to the facile reductive elimination of aryl- or aroylcobalt species from the Pd center. In contrast, $Pt(Ar)(OTf)(PPh_3)_2$ (Ar=Ph or *p*-Tol) reacted smoothly with $K[Co(CO)_4]$ in THF, and dinuclear complexes $(PPh_3)(CO)(Ar)Pt-Co(CO)_3(PPh_3)$ (**1a**: Ar=Ph, **1b**: Ar=*p*-Tol) were obtained as red crystals in high yields (**1a**: 84%, **1b**: 72%) after column chromatography (alumina, benzene) and recrystallization (benzene-hexane) (Eq. 3).[8] The molecular structure of **1a** was determined by the X-ray diffraction analysis.[9] The ORTEP drawing of **1a** is shown in Fig. 1. The Co atom occupies the cis position to the phenyl group (Pt1–Co1, 2.645(2) Å), and one PPh_3 ligand migrated from the Pt to the Co, and one CO ligand from the Co to the Pt. In accordance with this structure, the $^{31}P\{^1H\}$ NMR spectra of **1** showed two signals assignable to PPh_3 ligands on the Pt and Co atoms.[8]

$$\mathrm{Pt(Ar)(I)(PPh_3)_2} \xrightarrow[\text{- AgI}]{\text{AgOTf}} \xrightarrow[\text{- KOTf}]{\text{K[Co(CO)}_4]} \mathrm{(PPh_3)(CO)(Ar)Pt\text{-}Co(CO)_3(PPh_3)} \qquad (3)$$

1a, Ar=Ph; **1b**, Ar=*p*-Tol

Braunstein et al. have investigated the reaction of $MePt(OClO_3)(PPh_3)_2$ with $[Co(CO)_4]^-$ in toluene,[10)] but the product was identified to be $(PPh_3)_2MePt-Co(CO)_4$ on the basis of low temperature ^{31}P NMR data, and the ligand migration as in Eq. 3 was not mentioned.

On the other hand, the reaction of $Pd(Ph)(OTf)(PMe_3)_2$ with $K[Co(CO)_4]$ under CO gave $(PMe_3)_2(PhCO)Pd-Co(CO)_4$ (**2**) in 72% yield (Eq. 4) after column chromatography (alumina, benzene) and

$$\mathrm{Pd(Ar)(Br)(PMe_3)_2} \xrightarrow[\text{- AgBr}]{\text{CO, AgOTf}} \xrightarrow[\text{- KOTf}]{\text{K[Co(CO)}_4]} \mathrm{(PMe_3)_2(ArCO)Pd\text{-}Co(CO)_4} \qquad (4)$$

2, Ar=Ph

recrystallization (benzene–hexane). The IR spectrum of **2** shows an absorption at 1649 cm^{-1} assignable to the benzoyl group, and the ^1H and $^{31}P\{^1H\}$ NMR spectra indicated that two PMe_3 ligands are coordinated to the Pd atom in trans configuration.[11)] The structure of **2** was also determined by X-ray analysis[12)] and ORTEP drawing of **2** is shown in Fig. 2. As presumed by the spectroscopic data, a CO molecule has been inserted to the phenyl–palladium bond, and two PMe_3 ligands have trans configuration. Pd1–Co1 distance (2.7857(8) Å) is longer than that in $(Py)(PhNH\overline{N{=}C(Me)C_6H_4)P}dCo(CO)_4$ (Pd–Co 2.604(1) Å) in which the Co atom is located at the trans position to the nitrogen atom of the hydrazone ligand, and this is probably due to the stronger trans influence of the benzoyl group.[13)]

As a conclusion, this study not only provides a novel method for synthesis of aroylcobalt complexes but indicates that the ligand migration of the aryl (or aroyl) group from Pd to Co is an important pathway to realize the bimetallic catalysis in Eq. 1. In addition, heterodinuclear complexes **1** and **2** can be

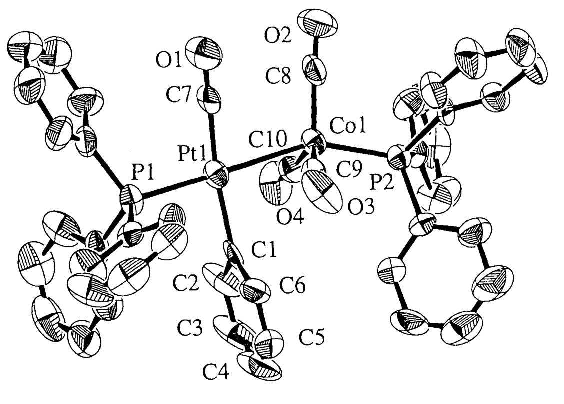


Fig. 1. ORTEP drawing of **1a**.

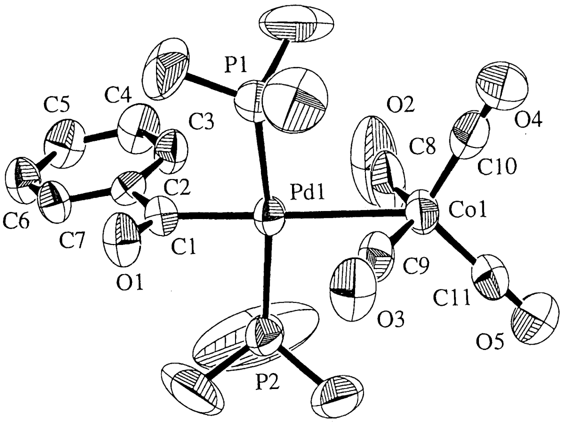


Fig. 2. ORTEP drawing of **2**.

considered as good models for an intermediate complex of such a ligand migration reaction,[14] although it is not clear at present which of the aryl and aroyl groups is transferred from Pd to Co in the actual catalytic reaction.

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8) **1a**: IR (KBr) 2049, 1977(m), 1925, and 1889 cm^{-1}; $^{31}P\{^1H\}$ NMR (C_6D_6) δ=18.0 (P–Pt, J_{Pt-P}=2969 Hz, J_{P-P}=59 Hz) and 64.9 (P–Co, J_{Pt-P}=222 Hz, J_{P-P}=59 Hz). Found: C, 56.95; H, 3.65%. Calcd for $C_{46}H_{35}O_4P_2CoPt$: C, 57.09; H, 3.65%. **1b**: IR (KBr) 2047, 1975(m), 1921, and 1887 cm^{-1}; ^1H NMR (C_6D_6) δ=2.27 (s, 3H), 6.82 (d, J=7.81 Hz, 2H), 6.9–7.7 (m, 30H), and 7.54 (d, J=7.81 Hz, 2H); $^{31}P\{^1H\}$ NMR (C_6D_6) δ=18.6 (P–Pt, J_{Pt-P}=2982 Hz, J_{P-P}=58 Hz) and 66.5 (P–Co, J_{Pt-P}=223 Hz, J_{P-P}=58 Hz). Found: C, 57.63; H, 3.88%. Calcd for $C_{47}H_{37}O_4P_2CoPt$: C, 57.50; H, 3.80%.
9) Crystallographic data of **1a**: $C_{46}H_{35}O_4P_2CoPt$, fw=967.75, monoclinic, $P2_1/c$, a=18.231(2), b=10.777(2), c=21.043(1) Å, β=90.338(7)°, V=4134.3(8) Å^3, Z=4, D_{calc}=1.555 g cm^{-3}, R=0.051, R_w=0.025 for 3929 obsevns ($I>3\sigma(I)$).
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11) **2**: IR (KBr) 2018, 1945, 1914, 1879, and 1649(m) cm^{-1}; ^1H NMR (C_6D_6) δ=0.87 (pseudo t, J=3.5 Hz, 18H), 7.10–7.18 (m, 3H), and 8.36 (d, J=7.1 Hz, 2H); $^{31}P\{^1H\}$ NMR (C_6D_6), δ=–23.9. Found: C, 38.32; H, 4.31%. Calcd for $C_{17}H_{23}O_5P_2CoPd$: C, 38.19; H, 4.34%.
12) Crystallographic data of **2**: $C_{17}H_{23}O_5P_2CoPd$, fw=534.65, monoclinic, $P2_1/c$, a=9.7753(8), b=14.3032(8), c=16.0758(7) Å, β=92.568(5)°, V=2245.4(2) Å^3, Z=4, D_{calc}=1.581 g cm^{-3}, R=0.037, R_w=0.026 for 3200 obsevns ($I>3\sigma(I)$).
13) G. Le Borgne, S. E. Bouaoud, D. Grandjean, P. Braunstein, J. Dehand, and M. Pfeffer, *J. Organomet. Chem.*, **136**, 375 (1977).
14) Thermal decomposition of **1b** was carried out in C_6D_6 under CO atmosphere at 50 °C, and formation of p-TolCOCo(CO)$_3$(PPh$_3$) (47% based on **1b** after 3 h) was disclosed by IR and ^1H NMR analyses. However, decomposition of **2** was not observed under the same conditions.

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