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Solid–gas carbonylation of aryloxide rhodium(I) complexes: stepwise reaction forming Vaska-type complexes

Kohtaro Osakada *, Hidetake Ishii

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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Abstract

Aryloxide rhodium(I) complexes Rh(OAr)(PPh₃)₃ (1a: Ar = C₆Cl₅, 1b: Ar = C₆F₅, 1c: Ar = C₆H₄–NO₂-4) react with CO in toluene solutions to produce Vaska-type complexes *trans*-Rh(OAr)(CO)(PPh₃)₂ (2a: Ar = C₆Cl₅, 2b: Ar = C₆F₅, 2c: Ar = C₆H₄–NO₂-4). Carbonylation of a similar complex with PMe₃ ligands, Rh(OC₆H₄–NO₂-4)(PMe₃)₃ (3c), also forms *trans*-Rh(OC₆H₄–NO₂-4)(CO)(PMe₃)₂ (4c). Molecular structures of the complexes are determined by X-ray crystallography and NMR spectroscopy. Complex 1a reacts with CO in the absence of solvent to produce a mixture of 2a and complex A, the latter of which shows the IR and $^{13}C{^{1}}H{}$ signals due to the carbonyl ligand at different positions from those of 2a. Addition of Et₂O to the above mixture turns it into analytically pure 2a. Carbonylation of 1b and 1c under the solvent-free conditions produces complexes B and C as the respective products of the solid–gas reaction. Recrystallization of B and C turns them into 2b and 2c, respectively. Complex 3c also reacts with CO in the solid state to form a mixture of 4c and complex D, although the latter complex is converted slowly into 4c even in the solid state. © 2004 Elsevier B.V. All rights reserved.

Keywords: Carbon monoxide; Rhodium; Carbonyl complex; Solid phases reaction

1. Introduction

Reactions of small molecules such as H_2 , acetylene and ethylene with the complexes of late transition metals are well known to cause coordination of these small molecules and activation of their bonds by the transition metal centers. Most of the reactions are carried out after dissolving the complexes in a solvent in order to make contact of the complex with gaseous compound smooth. A few papers reported the solid-gas reactions of transition metal complexes with small molecules [1–4]. These results suggest that the small molecules penetrate within the crystals or microcrystals of the solid complexes rapidly. Reactions of transition metal complexes in solutions are often triggered by dissociation of auxiliary ligands such as tertiary phosphines. The solid-gas reactions of a small molecule with transition metal complex are considered to proceed via the pathways other

than dissociative pathways in many cases because predissociation of the ligand in solution is accelerated by weak coordination of a solvent molecule to the vacant site. The intermediate complexes of the solid–gas reactions may have different structures from those in solution, and their structures and properties are of a significant interest.

In this paper, we report the reaction of CO with aryloxide rhodium(I) complexes with tertiary phosphine ligands, $Rh(OAr)(PPh_3)_3$ and $Rh(OAr)(PMe_3)_3$, in the absence of solvent. The products differ from those of the carbonylation in solution, $Rh(OAr)(CO)(PR_3)_2$, but they are easily converted into the Vaska-type complexes upon treatment with solvents. Reaction profiles, monitored by IR spectroscopy and the CP/MAS ¹³C NMR spectra of the products are also presented.

2. Results and discussion

Aryloxide rhodium complexes, $Rh(OAr)(PPh_3)_3$ (1a: Ar = C₆Cl₅, 1b: Ar = C₆F₅, 1c: Ar = C₆H₄-NO₂-4), were

^{*}Corresponding author. Tel.: +81-45-924-5222; fax: +81-45-924-5276.

E-mail address: kosakada@res.titech.ac.jp (K. Osakada).

prepared from the reaction of PPh₃ with $[Rh(\mu OAr)(cod)]_2$, and were characterized by NMR spectroscopy and elemental analyses (Eq. (1)).



The ${}^{31}P{}^{1}H$ NMR spectra of the complexes exhibit a doublet of triplets and a doublet of doublets in a 1:2 peak area ratio. These peaks are assigned to the P nucleus at *trans* position of the aryloxide ligand and those at *cis* positions, respectively. The reactions of



CO with complexes 1a-1c in toluene solution proceed smoothly at room temperature to afford Vaska-type complexes, *trans*-Rh(OAr)(CO)(PPh₃)₂ (2a: $Ar = C_6Cl_5$, **2b**: $Ar = C_6F_5$, **2c**: $Ar = C_6H_4$ -NO₂-4), via substitution of a PPh₃ ligand with CO, as shown in Eq. (2). IR spectra of 2a-2c exhibit the bands due to CO stretching at 1979, 1987 and 1985 cm⁻¹, respectively. Complex 2a-¹³CO containing ¹³CO labeled carbonyl ligand was prepared from the reaction of ¹³CO with **1a**, and showed the ¹³C{¹H} NMR peak of the carbonyl carbon at δ 190.07, which is accompanied by splitting due to Rh-C and P–C coupling (-70 °C). ${}^{13}C{}^{1}H$ NMR spectra of **2b**-¹³C and **2c**-¹³C at room temperature exhibit the signals at δ 189.93 and 189.60, respectively, although broadening of the signal prevents from determination of precise P-C coupling constants. These IR and NMR peak positions are in the range of already reported Vaska type complexes. Complex $Rh(OC_6H_4-NO_2-$ 4)(PMe₃)₃ (3c), prepared from the reaction of PMe₃ with $[Rh(\mu-OC_6H_4-NO_2-4)(cod)]_2$, also reacts with CO in toluene to afford the carbonyl complex, trans- $Rh(OC_6H_4-NO_2-4)(CO)(PMe_3)_2$ (4c) (Eq. (3)).



Fig. 1 shows molecular structures of 2a-2c and 4c determined by X-ray crystallography. Selected bond



Fig. 1. ORTEP drawings of (a) 2a, (b) 2b, (c) 2c, and (d) 4c at 50% ellipsoidal levels. Hydrogen atoms were omitted.

distances and angles are listed in Table 1. Rh–O–C bond angles (126–135°) and O–C bond distances (1.28–1.31 Å) are similar to those of the reported alkoxide and aryloxide complexes of late transition metals [5–9].

Solid–gas carbonylation of **1a** was conducted by introducing CO (1 atm) into a Schlenk flask containing the complex. Color of the solid changed from orange to offwhite, as shown in Fig. 2. IR and ${}^{13}C{}^{1}H{}$ NMR spectra of the product measured in the solid state revealed that it contained a mixture of Rh complex with a carbonyl ligand, **A**, and a smaller amount of **2a**. Addition of Et₂O to the solid mixture did not cause dissolution of it, but the solid recovered from the dispersion in Et₂O was composed of analytically pure **2a**.

Fig. 3 shows change of the IR spectra of the product of solid-gas reaction of CO with 1a measured in the absorbance mode. Benzophenone was added as an internal standard to estimate relative intensity of the carbonyl peaks. After 15 min from the beginning, a small peak appeared at 1979 cm^{-1} . The peak is at the same position as that of 2a, although it is broadened significantly compared with that of 2a prepared by the reaction in toluene solution and purified by recrystallization. After 30 min, growth of a peak at 1970 cm⁻¹ was observed. Relative peak intensity of the product to that of benzophenone (carbonyl stretching, 1659 cm⁻¹) indicated that the peak growth was ceased at 60 min after introducing CO. Thus, the reaction produces complex A that exhibits v(CO) peak at lower wavenumber than 2a. Similar solid-gas reactions of CO with 1b and with 1c

Table 1 Selected bond distances (Å) and angles (°)

	2a	2b	2c	4c	
Rh1–C1	1.829(6)	1.807(4)	1.829(9)	1.790(6)	
Rh1–O2	2.074(3)	2.061(3)	2.072(5)	2.089(4)	
Rh1–P1	2.324(1)	2.322(2)	2.335(2)	2.312(2)	
Rh1–P2	2.332(1)	2.321(2)	2.331(2)	2.315(2)	
C101	1.129(5)	1.145(4)	1.127(9)	1.154(7)	
O2–C2	1.304(5)	1.294(4)	1.302(8)	1.288(6)	
P1-Rh1-P2	174.81(5)	177.11(4)	172.88(8)	177.49(7)	
P1-Rh1-C1	88.7(2)	89.9(1)	90.9(2)	91.8(2)	
P1-Rh1-O2	92.1(1)	89.22(9)	86.6(1)	89.1(1)	
P2-Rh1-O2	89.4(1)	93.03(9)	94.8(1)	88.5(1)	
P2-Rh1-C1	89.2(2)	88.0(1)	87.8(2)	90.7(2)	
C1-Rh1-O2	172.8(2)	175.9(2)	177.0(3)	177.5(3)	
Rh1-C1-O1	178.4(5)	178.9(4)	178.2(8)	178.0(6)	
Rh1-O2-C2	135.0(3)	134.2(2)	130.5(4)	126.0(4)	



Fig. 2. Change of color of **1a** during the reaction with CO in the solid state.

produce the complexes with the CO ligand as a yellow paste and off-white solid, respectively. Fig. 4 shows change of the IR spectrum during the reactions of CO with **1b** and with **1c**. The peaks are observed at 1973 and 1975 cm⁻¹ which are different positions from Vaska-type complexes **2b** (1987 cm⁻¹) and **2c** (1985 cm⁻¹). The IR spectra of the products do not show the peak due to Vaska-type complexes throughout the reaction.

Fig. 5 shows the CP/MAS ¹³C{¹H} NMR spectrum of the product of the solid–gas reaction of ¹³CO with **1a**. A peak at δ 190 is assigned to the carbonyl ligand of **2b** formed via the solid–gas reaction and that formed during the measurement at high temperature. A larger signal at δ 274 is assigned to the complex **A**. The products from the solid–gas reaction of ¹³CO with **1b** and **1c** exhibit the signals at δ 271 and 275, which are assigned to **B** and **C**, respectively. These low magnetic field positions of the carbonyl carbon are not ascribed to bridging coordination of the carbonyl ligand but to low electron density of the carbon of the intermediates in the solid state because the IR frequencies at the CO stretching are within the range of non-bridging carbonyl ligand.



Fig. 3. IR spectra of 1a during the solid-gas reaction with CO.

We tentatively assign the penta-coordinated structure $Rh(OAr)(CO)(PPh_3)_3$ for the product of the solid–gas reactions because it is converted into Vaska-type complexes only by treating it with solvents. An ionic complex $[Rh(CO)(PPh_3)_3]^+OAr^-$ can be considered as the structure. Further evidences for the structures of A–C were not obtained. We examined a reaction of CO with single crystals of **1a** with expectation of the crystallographic study of the product, but the crystal lattices are not kept after the reactions. Reaction of PPh₃ with the Vaska-type complex **2a** does not cause change of the complex at all.



Fig. 4. IR spectra of (a) 2a and (b) 2b during the solid–gas reaction with CO.



Fig. 5. CP/MAS ¹³C NMR spectrum of A (67.5 MHz).

Solid–gas carbonylation of **3c** produces a mixture of Vaska-type complex **4c** and complex **D**, the latter of which shows the IR peak at lower position (1933 cm⁻¹) than **4c** (1962 cm⁻¹) at the initial stage of the reaction. Fig. 6 shows change of the IR spectrum during the reaction. After 5 days, the peak of **D** is observed in a similar intensity to that of **4c**. After 13 days, the ratio becomes smaller, and the peak is not detected after 23



Fig. 6. IR spectra of 3c during the solid-gas reaction with CO.

days. These results indicate that the initially formed complex **D** is turned into the final product 4c in the solid state and that the Vaska-type complex of the solid state reaction is formed via intermediate **D**. Low vapor pressure of PMe₃ seems to enhance the ligand substitution.

In summary, the solid–gas reaction of carbon monoxide with the aryloxide rhodium(I) complexes affords the complexes that can be transformed easily by addition of solvent into Vaska-type complexes by addition of solvent. The reactions are completed in a short period (15–60 min), indicating that penetration of CO within the solid and the chemical reaction in the solid state occurs rapidly.

3. Experimental

3.1. General, measurements and materials

All the manipulations were performed under nitrogen using standard Schlenk techniques. Solvents were distilled by usual method and stored under nitrogen. Other organic chemicals were purchased and used as received. $[Rh(\mu-OAr)(cod)]_2$ (Ar = C₆Cl₅, C₆F₅, C₆H₄–NO₂-4) were prepared from the reaction of ArOH with $[Rh(\mu-OMe)(cod)]_2$ [10] according to the literature describing the preparation of $[Rh(\mu-OPh)(cod)]_2$ [5,11]. IR spectra were recorded on a JASCO-IR 810 spectrophotometer. NMR spectra were obtained on JEOL EX-400 and Varian Mercury 300 spectrometers. Elemental analyses were carried out by a Yanagimoto Type MT-2 CHN autocorder.

3.2. Preparation of $Rh(OC_6Cl_5)(PPh_3)_3$ (1a)

To a toluene (10 ml) solution of $[Rh(OC_6Cl_5)(cod)]_2$ (236 mg, 0.25 mmol) was added PPh₃ (2.4 g, 9.2 mmol) at room temperature. The initially yellow dispersion was converted to an orange solution during heating the mixture for 2 h at 60 °C. The solvent was removed under vacuum. The produced solid was recrystallized from Et₂O–hexane to cause separation of an orange solid from the solution. The solid was collected by filtration, followed by washing with Et₂O, and dried in vacuo to afford **1a** as deep orange microcrystals (123 mg, 53%). ¹H NMR (CDCl₃, 400 MHz, r.t.): δ 7.45 (d, 6H, – C₆H₅), 7.65 (t, J = 6 Hz, 9H, –C₆H₅). ³¹P{¹H} NMR (benzene-d₆, 160 MHz, r.t.): δ 30.3 (dd, J(RhP) = 133Hz, J(PP) = 39 Hz), 51.1 (dt, J(RhP) = 199 Hz, J(PP) = 39 Hz).

3.3. Preparation of $Rh(OC_6F_5)(PPh_3)_3$ (1b)

To a toluene (10 ml) solution of $[Rh(OC_6F_5)(cod)]_2$ (270 mg, 0.34 mmol) was added PPh₃ (1.1 g, 4.1 mmol) at room temperature. PPh₃ was soon dissolved in the solvent to form an orange solution. The solution was stirred for 5 min at that temperature. The solvent was removed by evaporation. The resulted solid was recrystallized from Et₂O–hexane to give **1b** as a yellow– orange solid (309 mg, 84%). ¹H NMR (benzene-d₆, 300 MHz, r.t.): δ 6.85 (d, 6H, -C₆H₅), 7.73 (t, *J* = 7 Hz, 9H, -C₆H₅). ³¹P{¹H} NMR (benzene-d₆, 121 MHz, r.t.): δ 32.0 (dd, *J*(RhP) = 148 Hz, *J*(PP) = 41 Hz), 55.2 (dt, *J*(RhP) = 184 Hz, *J*(PP) = 41 Hz). *Anal.* Calc. for C₆₀H₄₅F₅OP₃Rh: C, 67.17; H, 4.23; F, 8.85. Found: C, 67.23; H, 4.43; F, 7.88%.

3.4. Preparation of $Rh(OC_6H_4-NO_2-p)(PPh_3)_3$ (1c)

To a toluene (10 ml) solution of $[Rh(OC_6H_4-NO_2$ $p(\text{cod})_{2}$ (153 mg, 0.22 mmol) was added PPh₃ (604 mg, 2.6 mmol) at room temperature. PPh₃ was soon dissolved to form an orange solution. After stirring the solution for 5 min, the solvent was removed by evaporation. The obtained solid was washed with Et₂O and dried in vacuo to give 1c as yellow-orange crystals (369 mg, 79%). Recrystallization from THF/ hexane afforded single crystals. ¹H NMR (benzene-d₆, 300 MHz, r.t.): δ 6.43 (d, 2H, $-C_6H_4NO_2-p$), 6.80 (d, 6H, $-C_6H_5$), 7.56 (t, J = 6 Hz, 9H, $-C_6H_5$), 8.16 (d, 2H, $-C_6H_4NO_2-p$). ³¹P{¹H} NMR (benzene-d₆, 160 MHz, r.t.): δ 31.6 (dd, J(RhP) = 153 Hz, J(PP) = 39Hz), 51.0 (dt, J(RhP) = 176 Hz, J(PP) = 39 Hz). Anal. Calc. for C₆₀H₄₉NO₃P₃Rh: C, 70.11; H, 4.80; N, 1.36. Found: C, 69.91; H, 6.26; N, 1.57%.

3.5. Reaction of CO with $Rh(OC_6Cl_5)(PPh_3)_3$ (1a) in solution

Complex **1a** (123 mg, 0.11 mmol) was dissolved in toluene (3 ml) in a Schlenk flask (20 ml). After degassing the system, CO (1 atm) was introduced, which caused change of color of the solution from orange to yellow soon. After 5 min, the solvent was removed by evaporation. The obtained solid product was washed with Et₂O and dried in vacuo to give Rh(OC₆Cl₅)(CO)-(PPh₃)₂ (**2a**) (65 mg, 67%). Recrystallization from THF/ hexane afforded yellow crystals. ³¹P{¹H} NMR (CDCl₃, 160 MHz, r.t.): δ 30.5 (d, *J*(RhP) = 137 Hz). IR (KBr pellet): *v*(CO) 1979 cm⁻¹.

Similar reactions of CO with **1b** and with **1c** in toluene solution afforded $Rh(OC_6F_5)(CO)(PPh_3)_2$ (**2b**) (70%) and $Rh(OC_6H_4-NO_2-p)(CO)(PPh_3)_2$ (**2c**) (76%), respectively.

Data of **2b** are as follows. ³¹P{¹H} NMR (benzened₆, 121 MHz, r.t.): δ 29.6 (d, J(RhP) = 135 Hz). IR (KBr pellet): v(CO) 1987 cm⁻¹. *Anal.* Calc. for C₄₃H₃₀-F₅O₂P₂Rh: C, 61.60; H, 3.61; F, 11.33. Found: C, 61.96; H, 4.13; F, 10.97%.

Data of **2c** are as follows. ${}^{31}P{}^{1}H$ NMR (benzened₆, 121 MHz, r.t.): δ 29.4 (d, J(RhP) = 135 Hz). IR (KBr pellet): v(CO) 1985 cm⁻¹.

3.6. Preparation of $Rh(OC_6H_4-NO_2-p)(PMe_3)_3$ (3c)

Addition of PMe₃ (0.5 ml, 4.8 mmol) to a toluene (10 ml) dispersion of [Rh(OC₆H₄–NO₂-*p*)(cod)]₂ (542 mg, 0.78 mmol) caused change of color of the reaction mixture from yellow to orange. After stirring for 5 min, the solvent was removed by evaporation. The obtained solid product was washed with hexane and dried in vacuo to give **3c** as a deep yellow solid (840 mg, 100%). ³¹P{¹H} NMR (benzene-d₆, 160 MHz, r.t.): δ –8.2 (dd, *J*(RhP) = 86 Hz, *J*(PP) = 27 Hz), 5.2 (dt, *J*(RhP) = 113 Hz, *J*(PP) = 27 Hz). *Anal.* Calc. for C₁₅H₃₁NO₃P₃Rh: C, 38.40; H, 6.66; N, 2.98. Found: C, 38.14; H, 6.94; N, 2.85%.

3.7. Reaction of CO with $Rh(OC_6H_4-NO_2-p)(PMe_3)_3$ (3c) in solution

A solution of Rh(OC₆H₄–NO₂-*p*)(PMe₃)₃ (**3c**) (34 mg, 0.072 mmol) in toluene (3 ml) was prepared in a Schlenk flask (20 ml). After degassing the system, CO (1 atm) was introduced at room temperature. The solution was soon turned from orange to yellow. After 5 min, the solvent was removed by evaporation. The obtained solid was washed with Et₂O and hexane, and dried in vacuo to afford Rh(OC₆H₄–NO₂-*p*)(CO)(PMe₃)₂ (**4c**) (19 mg, 62%). Recrystallization from acetone/hexane afforded yellow single crystals.

 ${}^{31}P{^{1}H}$ NMR (CDCl₃, 160 MHz, r.t.): δ -8.4 (d, J(RhP) = 121 Hz). IR (KBr pellet): v(CO) 1964 cm⁻¹. *Anal.* Calc. for C₁₃H₂₂NO₄P₂Rh: C, 37.07; H, 5.26; N, 3.33. Found: C, 37.03; H, 5.38; N, 3.20%.

3.8. Solid–gas reaction of CO with $Rh(OC_6Cl_5)(PPh_3)_3$ (1a)

Rh(OC₆Cl₅)(PPh₃)₃ (**1a**) (335 mg, 0.29 mmol) was transferred to a Schlenk flask (20 ml). After degassing, CO (1 atm) was introduced. The orange solid was gradually turned to off-white. The solid product was composed of **A** and **2a** based on the IR and CP/MAS ${}^{13}C{}^{1}H$ NMR spectra.

The product was washed with Et₂O and dried in vacuo to give **2a** as a yellow solid (208 mg, 79%). IR (KBr pellet): v(CO) 1979 cm⁻¹. ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz, -70 °C): δ 190.07 (dt, J(RhC) = 70 Hz, J(PC) = 18Hz), 136.94, 136.83, 134.57, 133.80 (d, J = 27 Hz), 133.69, 131.17, 130.94, 130.73, 130.62, 129.05, 128.79, 128.71, 128.61. 128.43, 121.07. ³¹P{¹H} NMR (CDCl₃, 160 MHz, r.t.): δ 30.5 (d, J (RhP) = 137 Hz). ³¹P{¹H} NMR (¹³CO-enriched sample, CD₂Cl₂, 160 MHz, -70 °C): δ 34.2 (d, J(RhP) = 135 Hz, J(CP) = 18 Hz). *Anal.* Calc. for C₄₃H₃₀Cl₅O₂P₂Rh: C, 56.09; H, 3.28; Cl, 19.25. Found: C, 55.88; H, 3.94; Cl, 18.73%.

3.9. Solid–gas reaction of CO with $Rh(OC_6F_5)(PPh_3)_3$ (1b)

A Schlenk flask (20 ml) containing **1b** (39 mg, 0.036 mmol) was evacuated by vacuum pump. CO (1 atm) was introduced to the flask at room temperature. Yellow orange solid was gradually turned into a yellow paste (**B**). The product **B** was recrystallized from Et_2O (2 ml)/hex-

ane (10 ml) to give **2b** as a yellow solid (27 mg, 80%). ³¹P{¹H} NMR (benzene-d₆, 121 MHz, r.t.): δ 29.6 (d, J(RhP) = 135 Hz). ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz, 25 °C): δ 189.93 (d, J(RhC) = 66 Hz, J(PC) was not observed due to peak broadening). IR (KBr pellet): ν (CO) 1987 cm⁻¹. *Anal*. Calc. for C₄₃H₃₀F₅O₂P₂Rh: C, 61.60; H, 3.61; F, 11.33. Found: C, 61.87; H, 3.87; F, 11.53%.

3.10. Solid-gas reaction of CO with $Rh(OC_6H_4-NO_2-p)(PPh_3)_3$ (1c)

A Schlenk flask (20 ml) containing $Rh(OC_6H_4-NO_2-p)(PPh_3)_3$ (1c) (8 mg, 0.01 mmol) was degassed at room temperature. Introducing CO (1 atm) at room temperature turned the orange solid to form an off-white solid C.

The solid product **C** was recrystallized from Et₂O(2 ml)/hexane(10 ml) to give **2b** as a yellow solid (6.7 mg, 85%). ³¹P{¹H} NMR (benzene-d₆, 121 MHz, r.t.): δ 29.4 (d, *J* (RhP) = 135 Hz). ¹³C{¹H} NMR (CD₂Cl₂, 125 MHz, 25 °C): δ 189.60 (d, *J*(RhC) = 70 Hz, *J*(PC) was not observed due to peak broadening). IR (KBr pellet): ν (CO) 1985 cm⁻¹. *Anal*. Calc. for C₄₃H₃₄NO₄P₂Rh: C, 65.08; H, 4.32; N, 1.76. Found: C, 64.95; H, 4.51; N, 1.70%.

3.11. Solid–gas reaction of PPh₃ with $Rh(OC_6Cl_5)$ (CO)(PPh₃)₂ (**3a**)

Finely ground PPh₃ (30 mg, 0.11 mmol) was mixed with complex **3a** (30 mg, 0.026 mmol) at room temperature. The IR peak at 1979 cm⁻¹ did not change even after 5 days. Analogous reaction of CO with **A** without solvent did not cause change of the IR peaks.

Table 2						
Crystal	data	and	details	of	structure	refinement

	2a	2b	2c	4c
Formula	$C_{43}H_{30}Cl_5O_2P_2Rh$	$C_{43}H_{30}F_5O_2P_2Rh$	$C_{43}H_{34}NO_4P_2Rh$	$C_{13}H_{22}NO_4P_2Rh$
Molecular weight	920.83	838.56	793.60	421.18
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	<i>P</i> 1 (no. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (no. 14)
a (Å)	13.304(3)	12.810(9)	15.748(4)	6.018(3)
b (Å)	19.713(6)	14.117(8)	14.701(4)	18.247(4)
<i>c</i> (Å)	15.641(3)	11.899(7)	17.414(3)	16.428(3)
α (°)		92.00(5)		
β (°)	106.49(1)	113.99(5)	112.92(1)	92.67(3)
γ (°)		74.22(5)		
V (Å ³)	3933	1885	3714	1802
Ζ	4	2	4	4
$\mu (cm^{-1})$	0.891	0.598	0.589	1.235
F(000)	1856	848	1624	1024
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.555	1.477	1.419	1.833
Crystal size (mm)	$0.5\times0.3\times0.2$	$0.7 \times 0.5 \times 0.3$	0.2 imes 0.2 imes 0.2	0.3 imes 0.1 imes 0.1
2θ range (°)	5.0-55.0	5.0-50.0	5.0-55.0	5.0-55.0
Number of unique reflections ^a	9299	8673	8866	4273
Number of used reflections	5699	6460	2845	2378
Number of variables	478	478	460	190
R	0.041	0.042	0.061	0.041
R_w	0.034	0.038	0.050	0.031
Goodness-of-fit	2.26	2.94	2.29	1.74

 $^{\mathrm{a}}I > 3\sigma(I).$

3.12. Solid–gas reaction of CO with $Rh(OC_6H_4-NO_2-p)-(PMe_3)_3$ (3c)

A Schlenk flask (20 ml) containing $Rh(OC_6H_4-NO_2-p)(PMe_3)_3$ (**3c**) (71 mg, 0.15 mmol) was degassed by a vacuum pump. Introduction of CO (1 atm) into the flask caused change of deep yellow solid to a pale yellow solid. After 5 days, the product is a mixture of **4c** and **D** in almost equal amounts. After 23 days, the IR spectrum indicates the presence of **4c** only.

The solid product obtained after the reaction for 5 h was washed with Et₂O and hexane, and dried in vacuo to give Rh(OC₆H₄–NO₂-*p*)(CO)(PMe₃)₂ (**4c**) (30 mg, 47%). ³¹P{¹H} NMR (CDCl₃, 160 MHz, r.t.): δ –8.3 (d, J(RhP) = 121 Hz). IR (KBr pellet): v(CO) 1966 cm⁻¹. *Anal.* Calc. for C₁₃H₂₂NO₄P₂Rh: C, 37.07; H, 5.26; N, 3.33. Found: C, 37.25; H, 5.44; N, 3.26%.

3.13. X-ray crystallography

Structural parameters of the crystals and results of refinement are summarized in Table 2. X-ray data were collected at 23 °C on a Rigaku AFC-5R automated diffractometer and monochromated MoK α radiation ($\lambda = 0.71073$ Å). Crystallographic data (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication no. CCDC 230246-230249. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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