Regio- and Stereoselective Hydroformylation of Glucal Derivatives with Rhodium Catalysts

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The hydroformylation of the differently protected glucal derivatives 3,4,6-tri-*O*-acetyl-D-glucal, 3,4,6-tri-*O*-benzyl-D-glucal and 3,4,6-tri-*O*-methyl-D-glucal was carried out with rhodium catalytic systems, and 2-formyl derivatives were obtained as the main products in yields of 58%, 68%, and 55% respectively, when $[Rh_2(\mu\text{-OMe})_2(COD)_2]$/$P(O\text{-}o\text{-}^tBuC_6H_4)_3$ was used. The bulky phosphite needs to be used as auxiliary ligand to achieve the hydroformylation of these highly hindered cyclic olefins. A mechanistic cycle is proposed which explains the regio- and stereoselectivity of the reaction. The mononuclear rhodium complex *trans*-$[RhCl(CO)(P(O\text{-}o\text{-}^tBuC_6H_4)_3)_2]$ was isolated at the end of the catalytic reaction by breaking the dinuclear complexes used as catalyst precursors. To confirm the characterization of *trans*-$[RhCl(CO)(P(O\text{-}o\text{-}^tBuC_6H_4)_3)_2]$, a separate synthesis was carried out which isolated crystals suitable for an X-ray determination.

Introduction

Hydroformylation is a well-known industrial process which has recently attracted the attention of researchers with a view to functionalizing complex molecules.[1] The increasing interest in *C*-glycosides[2] and *C*-disaccharides[3] prompted us to explore the hydroformylation of glycals as a direct method of obtaining 2-deoxy-1-*C*-formyl glycosides, which are useful intermediates in their synthesis. Rosenthal[4] has studied the hydroformylation of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) using $[Co_2(CO)_8]$ as catalyst and has obtained an α/β mixture of the 1-hydroxymethyl-2-deoxy carbohydrates **2** and **3** in drastic conditions of pressure and temperature. When the gas consumption was strictly controlled, aldehydes **4** and **5** were preferentially obtained,[5] but always as an α/β mixture (Scheme 1).

The hydroformylation of glycals involves an interesting problem of chemo-, regio-, and stereoselectivity. Rhodium catalysts are more active than cobalt catalysts, which means that the pressure and temperature can be lower and that the selectivity can be controlled better than for cobalt catalysts under milder conditions.

Since the first attempts at the hydroformylation of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) using $[RhH(CO)(PPh_3)_3]$[6] (**6**) or the dinuclear precursors $[Rh_2(\mu\text{-S-}^tBu)_2(CO)_2(PPh_3)_2]$[7] (**7**) and $[Rh_2(\mu\text{-}S(CH_2)_3NMe_2)_2(COD)_2]$[8] (**8**) as catalysts failed, a systematic study was made of the hydroformylation of 3,4-dihydro-2*H*-pyran (**9**) and 2,3-dihydrofuran (**10**), which can be considered as simple glycal models. The 2,3-dihydrofuran was easily hydroformylated under mild conditions with **6** and **7** and in the presence of PPh_3, while the 3,4-dihydro-2*H*-pyran was hydroformylated in very low yields even in more drastic conditions.[9,10] Only when the tris-*ortho*-*tert*-butylphenyl phosphite[11] (**11**) was used as auxiliary ligand could the compound **9** be hydroformylated to give

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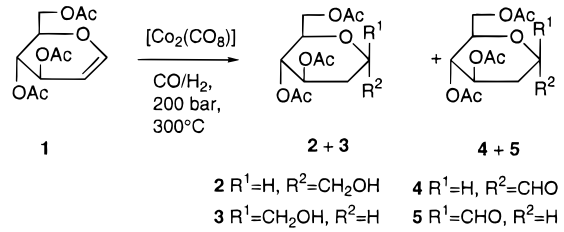
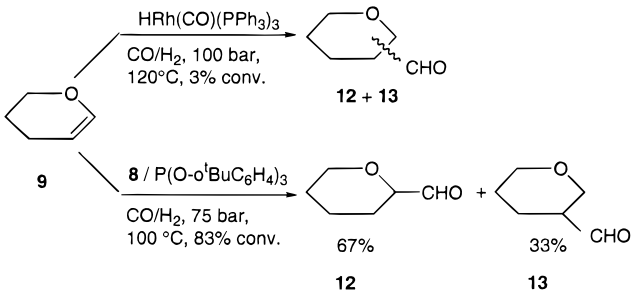
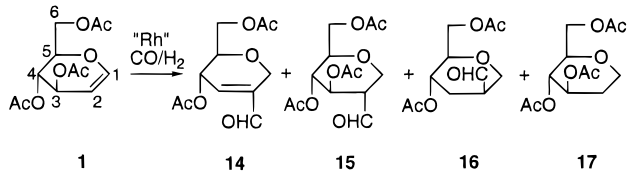
Scheme 1



Scheme 2



Scheme 3



a mixture of aldehydes **12** and **13**[9] (Scheme 2). Here we show that glucal derivatives can be hydroformylated using different rhodium precursors in the presence of the bulky phosphite **11**.

Results and Discussion

Hydroformylation of 3,4,6-Tri-*O*-acetyl-D-glucal. The 3,4,6-tri-*O*-acetyl-D-glucal (**1**) was hydroformylated using the catalytic system $[Rh_2(\mu\text{-}S(CH_2)_3NMe_2)(COD)_2]$/$P(O\text{-}o\text{-}^tBuC_6H_4)_3$ giving a mixture of aldehydes **14**, **15**, and **16**, together with some amounts of the hydrogenation product **17**[12] (Scheme 3).

Compounds **14**, **15**, and **17** were separated from the reaction mixture, and their structures were determined by spectroscopic methods. The most significant spectroscopic data (Table 1) for compound **14** are (a) the signals at 9.50 ppm in ^{1}H NMR and at 190.6 in ^{13}C NMR which confirm the presence of the formyl group, (b) the presence of only two methyl groups of acetyl groups at 2.12 and 2.14 ppm in ^{1}H NMR, (c) the signals at 6.72 ppm in ^{1}H NMR and at 141.6 ppm (CH) and 142.5 (C) in ^{13}C NMR which indicate the presence of a trisubstituted double bond, which must be formed by eliminating an OAc group, and (d) the signals at 4.58 and 4.35 ppm in ^{1}H NMR with a geminal coupling constant (J = 17 Hz), which indicate that these protons are in a carbon bonded to oxygen. Therefore this carbon was assigned as C_1.

The NMR spectroscopy of **15** (Table 1) shows (a) the signal at 197.2 in ^{13}C NMR and at 9.54 ppm in ^{1}H NMR which is coupled with H_2 (J = 2.7 Hz), (b) three acetyl groups at 1.98, 1.99, and 2.11 ppm in ^{1}H NMR which show that neither elimination nor substitution has taken place, and (c) the signal at 2.99 ppm in ^{1}H NMR attributed to H_2 is coupled to the signal at 3.48 ppm (H_{1axial}, J = 11.3 Hz) which shows that H_2 must be in an axial position.

Compound **16** could not be separated and purified by usual chromatographic techniques, and it was derivatized to the corresponding 2,4-dinitrophenylhydrazone, which was then separated by TLC. The structure of the 2,4-dinitrophenylhydrazone derived from **16** was determined taking into account the following ^{1}H NMR spectroscopic data (Table 1): (a) there are only two acetate groups at 2.00 and 2.07 ppm, (b) there are two pairs of signals (other than H_6, $H_{6'}$) at 3.79/4.10 ppm (H_{1e}, H_{1a}) and at 1.16/2.72 ppm (H_{3e},H_{3a}) which have geminal coupling constants, (J = 12 and 11 Hz, respectively), and (c) H_{1a}, H_{3a}, and H_{3e} have small coupling constants which show that this proton is in an equatorial or pseudoequatorial position.

The resulting regioselectivity is in contrast with the regioselectivity obtained when a cobalt catalyst was used. It is also in contrast with the one obtained in similar conditions in the hydroformylation of **9**, where the formyl group was mainly bonded to C_1. This group is now bonded to C_2, the carbon double bond with the highest electron density.[9,13] In an attempt to improve the yield and the selectivity of the process we made a systematic study of the reaction conditions.

First, we analyzed how selectivity varied with reaction time and we observed that there was a regular increase in the percentage of compounds **14** and **16** (entries 1 and 2, Table 2, Figure 1). On the other hand, compound **15** reached 14% in 3 h and then decreased, which suggests that it was converted into the elimination product **14**. In fact, the percentage of **14** + **15** was almost constant throughout the reaction. The yield and the selectivity did not change significantly when the temperature was increased or decreased (entries 3 and 4, respectively), but above 130 °C and below 80 °C the catalyst was not active. When the pressure was 40 or 90 bar (entries 5 and 6), conversions were low.

When toluene was used as the solvent, only traces of the side product **16** were obtained, although significant quantities of the hydrogenation product remained (entry 8). On the other hand, when THF, dioxane, and glycol dimethyl ether were used as the solvent, the selectivity observed was similar to the one obtained when 1,2-dichloroethane was used, but the reaction rate was slightly slower, in all the cases.

In a previous study, we attributed the differences in the hydroformylation of 2,3- and 2,5-dihydrofuran when $P(OPh)_3$ (cone angle = 128°) and $P(O\text{-}o\text{-}^tBuC_6H_4)_3$ (cone angle = 175°) were used as auxiliary ligands to steric rather than electronic effects.[9] To confirm this, we chose $P(o\text{-}MeC_6H_4)_3$ as the auxiliary ligand because it is a phosphine with a large cone angle (194°).[14] The very low conversions obtained in the hydroformylation of **1**

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Table 1. Selected ^{1}H and ^{13}C NMR δ Data (in ppm) of Compounds 14, 15, 16, and 22a[a]

	^{1}H NMR δ/(*J*)								^{13}C NMR
compd	CHO	H_{1e}	H_{1a}	H_{2e}	H_{2a}	H_{3e}	H_{3a}	H_4	CHO
14[b]	9.50 (s)	4.58 (ddd) (17, 2.2, 2.2)	4.35 (ddd) (17, 2.7, 2.7)	–	–	6.72 (q) (2.7, 2.7, 2.2)		5.50 (dq) (8.4, 2.7, 2.7, 2.2)	190.6
15	9.54 (d) (2.7)	4.00−4.25 (m)	3.40−3.60 (m)	–	2.99 (ddt) (17, 17, 8, 2.7)	–	5.22 (dd) (17, 14)	4.95 (dd) (14, 11)	197.2
16[c]	–	4.10 (d) (12)	3.79 (dd) (12, 3.3)	2.91 (td) (5.4, 3.3, 3.3)	–	2.72 (dd) (11, 4.4)	1.16 (ddd) (11, 10.3, 5.4)	5.12 (ddd) (10.3, 10, 4.4)	–
22a	9.70 (s)	–	3.83 (dd) (12.5, 5.2)	2.42 (td) (12.5, 5, 2.5)	1.54 (dt) (12.5, 12.5, 11.5)	–			201.2

[a] Sugar numbering has been used for C and H. See Scheme 3. [b] Double-bond carbons appear at 141.6 and 142.5 ppm. [c] As 2,4-dinitrophenylhydrazone derivative.

Table 2. Hydroformylation of 3,4,6-Tri-*O*-acetyl-D-glucal (1) with the Catalytic System $[Rh_2(\mu\text{-}S(CH_2)_3NMe_2)(COD)_2]/P(O\text{-}o\text{-}^tBuC_6H_4)_3$[e]

entry no.	solvent	pressure (bar)	temp. (°C)	time (h)	conversion[a] (%)	**14**[b]	**15**[b]	**16**[b]	**17**[b]
1	$Cl_2C_2H_4$	75	120	3	16	17	14	–	12
2	$Cl_2C_2H_4$	75	120	24	84	34	6	27	15
3	$Cl_2C_2H_4$	60	130	24	94	34	8	31	12
4	$Cl_2C_2H_4$	60	110	24	93	30	6	26	13
5	$Cl_2C_2H_4$	40	120	24	38	16	20	27	6
6	$Cl_2C_2H_4$	90	120	24	68	33	13	32	7
7	$Cl_2C_2H_4$[c]	60	120	24	72	31	13	30	10
8	toluene	60	120	24	80	40	3	trace	17
9	$Cl_2C_2H_4$[d]	60	120	24	15	4	20	3	17

[a] Percentage of transformed product. [b] Percentage of the products identified, related to the products of the reaction detected by GC. [c] $P_{CO}/P_{H_2} = 3/2$. [d] Auxiliary ligand P(*o*-$MeC_6H_4)_3$. [e] Standard conditions: substrate (5 mmol), auxiliary ligand (0.5 mmol), precursor of catalyst (0.05 mmol), solvent: 15 mL, $P_{CO}/P_{H_2} = 1/1$.

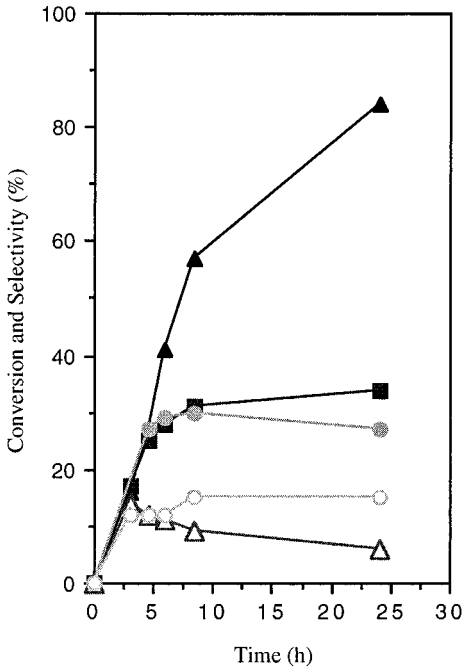


Figure 1. Evolution of the hydroformylation of 3,4,6-tri-*O*-acetyl-D-glucal. (▲) Conversion, (●) selectivity on **14**, (■) selectivity on **15**, (○) selectivity on **16**, (△) selectivity on **17** (in %).

(entry 9) showed that electronic factors of the auxiliary ligand also affect the activity of the catalytic systems in the hydroformylation of hindered olefins.

The very narrow range of conditions in which the catalytic systems were active and the slight variations observed in the yield and selectivity prevented us from making a more extensive study. On the other hand, the elimination product **14** and the aldehyde **16** may have been obtained because of the presence of the acetates as protecting group, which are good leaving groups, and a basic amino group in the catalyst. So, to increase the selectivity we decided to use other nonbasic catalytic precursors and to change the protecting groups.

Initially, we focused on the fact that all the experiments performed with the catalytic system $[Rh_2(\mu\text{-}S(CH_2)_3NMe_2)(COD)_2]/P(O\text{-}o\text{-}^tBuC_6H_4)_3$ in chlorinated solvents afforded the mononuclear rhodium complex *trans*-$[RhCl(CO)(P(O\text{-}o\text{-}^tBuC_6H_4)_3)_2]$ (**18**) at the end of the reaction. This suggests that the active species is mononuclear and probably similar to the isolated species. On the other hand, it is known that the dinuclear rhodium complex $[Rh_2(\mu\text{-}OMe)_2(COD)_2]$ (**19**) easily gives monuclear species under catalytic conditions. Moreover, this catalytic precursor has no basic groups in its structure, which makes it an attractive catalytic precursor for the hydroformylation of glucal derivatives.

The catalytic precursor **19** was, in general, slightly less active than **8** and required longer reaction times (entries 1 and 2, Table 3). However, as far as selectivity is concerned, the 2-formyl derivative **15** was obtained in higher percentages than when catalytic system **8**/P(O-*o*-$^tBuC_6H_4)_3$ was used. The yield and selectivity were not significantly affected by pressure changes (entries 3 and 4), but the percentage of elimination and hydrogenation products were affected by changes in the temperature and in the solvent (entries 5 and 6). One important difference is that when precursor **19** was used, compound **16** was not obtained.

The complex *trans*-$[RhCl(CO)(P(O\text{-}o\text{-}^tBuC_6H_4)_3)_2]$[9] (**18**) was not a good precursor of the catalyst in the hydroformylation of 3,4,6-tri-*O*-acetyl-D-glucal, and the main product observed after 48 h was the hydrogenated product **17** (entry 8).

The presence of halogens in the reaction mixture is known to inhibit the catalytic reaction.[15] Et_3N was added to scavenge hydrogen chlorine (entry 9), but the

Table 3. Hydroformylation of 3,4,6-Tri-*O*-acetyl-D-glucal (1) with the Catalytic System [$Rh_2(\mu$-OMe)$(COD)_2$] (19)/P(O-*o*-^{t}Bu$C_6H_4)_3$[f]

entry no.	solvent	pressure (bar)	temp. (°C)	time (h)	conversion[a] (%)	**14**[b]	**15**[b]	**16**[b]	**17**[b]
1	$Cl_2C_2H_4$	55	100	24	54	20	58	–	7
2	$Cl_2C_2H_4$	55	100	48	90	22	54	–	8
3	$Cl_2C_2H_4$	70	100	48	91	19	58	–	8
4	$Cl_2C_2H_4$	45	100	48	94	21	54	–	8
5	$Cl_2C_2H_4$	55	130	48	92	37	5	trace	23
6	toluene	55	100	48	94	37	5	trace	37
7	$Cl_2C_2H_4$[c]	55	100	48	14	11	14	–	5
8	$Cl_2C_2H_4$[d]	55	100	48	44	1	23	–	76
9	$Cl_2C_2H_4$[e]	55	100	48	37	7	4	–	19

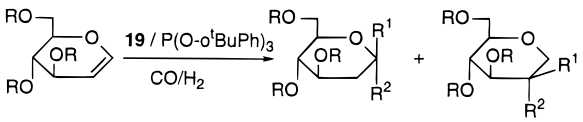
[a] Percentage of transformed product. [b] Percentage of the products identified, related to the products of the reaction detected by GC. [c] Auxiliary ligand P(*o*-$MeC_6H_4)_3$. [d] Precursor of catalyst: [RhCl(CO)(P(O-*o*-^{t}Bu$C_6H_4)_3)_2$]. [e] Precursor of catalyst: [RhCl(CO)(P(O-*o*-^{t}Bu$C_6H_4)_3)_2$] + 0.5 mmol of NEt_3. [f] Standard conditions: substrate (5 mmol), auxiliary ligand (0.5 mmol), precursor of catalyst (0.05 mmol), solvent: 15 mL, $P_{CO}/P_{H_2} = 1/1$.

Table 4. Hydroformylation of 3,4,6-Tri-*O*-benzyl-D-glucal (20a) and 3,4,6-Tri-*O*-methyl-D-glucal (20b) with the Catalytic System 19/P(O-*o*-^{t}Bu$C_6H_4)_3$[c]

entry no.	sub.	solvent	conv.[a] (%)	**21**[b]	**22**[b]	**23**[b]
1	**20a**	$Cl_2C_2H_4$	99	9	10	68
2	**20a**	toluene	99	9	10	39
3	**20b**	$Cl_2C_2H_4$	99	11	16	55

[a] Percentage of transformed product. [b] Percentage of the products identified, related to the products of the reaction detected by GC. [c] Standard conditions: substrate (5 mmol), auxiliary ligand (0.5 mmol), precursor of catalyst (0.05 mmol), solvent 15 mL, $P_{CO}/P_{H_2} = 1/1$, $T = 100$ °C, $P = 50$ bar, $t = 9$ h.

Scheme 4



20a R=$PhCH_2$ **21a,b** R^1=H, R^2=CHO **23a,b** R^1=H, R^2=CHO
20b R=Me **22a,b** R^1=CHO, R^2=H **24a,b** R^1=CHO, R^2=H

hydrogenated product was still the main product obtained. This proves that the complex **18** is not the active species and that it is probably formed when the catalytic reaction has finished.

Hydroformylation of 3,4,6-Tri-*O*-benzyl-D-glucal (20a) and 3,4,6-Tri-*O*-methyl-D-glucal (20b) with the Catalytic System [Rh2(μ-OMe)(COD)2]/P(O-*o*-^{t}Bu$C_6H_4)_3$. The use of ether type protecting groups in glucal prevents the secondary products **14** and **16** from being formed. Thus, when 3,4,6-tri-*O*-benzyl-D-glucal (**20a**) was hydroformylated in 1,2-dichloroethane, using the catalytic system **19**/P(O-*o*-^{t}Bu$C_6H_4)_3$ under the conditions shown in Table 4, the conversion was completed in 9 h, and only aldehydes were obtained. Compounds **21a**, **22a**, and **23a** were identified (Scheme 4), but five aldehyde signals were detected. However, the three products identified make up 87% of the total products. Compound **23a**, the 2-formyl derivative, was obtained in the highest percentage, 68% (entry 1, Table 4).

When toluene was used as the solvent, the selectivity after 3 h was similar to that obtained in 1,2-dichloroethane, with a conversion of 65%. After 9 h the conversion was complete. However, the percentage of compound **23a** decreased to 39% (entry 3, Table 4). A small amount of reaction mixture was purified by TLC, and pure compound **22a** was isolated. The most significant spectroscopic NMR data (Table 1) which supported this structure were (a) an aldehydic proton at 9.70 ppm in the ^{1}H NMR and at 201.2 ppm in the ^{13}C NMR, (b) the presence of three benzyl groups, and (c) the appearance of two signals at 2.42 and 1.54 ppm with a $^2J = 12.5$ Hz. If the δ value is taken into account, these signals can be assigned to a CH_2 group which is not bonded to oxygen ($\delta = 31.3$ ppm in ^{13}C NMR), so they are bonded to C_2, and (d) the signal at 1.54 ppm has two coupling constants of 11 Hz, which show that the neighboring protons H_1 and H_3 are axial; therefore, the formyl group must be equatorial in C_1.

The 2,4-dinitrophenylhydrazone derivatives of the reaction mixure products were prepared and the hydrazone of the main product **23a** was isolated. In the ^{1}H NMR spectrum the hydrazone derivative of **23a** has a signal at 2.85 ppm with four coupling constants. Double resonance experiments showed that two of these were trans-diaxial, that one was an axial−equatorial coupling, and that the fourth coupled with the imino proton. This proton was assigned as H_2, and so the formyl group at position 2 is equatorial.

The hydroformylation of 3,4,6-tri-*O*-methyl-D-glucal **20b** with the catalytic system **19**/P(O-*o*-^{t}Bu$C_6H_4)_3$ gave a quantitative conversion in aldehydes after 9 h under the conditions shown in Table 4. In this case also, the main product was the 2-formyl derivative **23b** of the gluco configuration. Neither the aldehydes nor the 2,4-dinitrophenylhydrazone derivatives of the reaction products could be purified by usual chromatographic techniques.

Nevertheless, using GC-MS analysis, compounds with the formyl group at C_1 and C_2 were differentiated. While the mass spectra of two compounds show the loss of the •CHO and CO fragments from their molecular ions, the mass spectrum of the major compound does not. It has been described[16] that substituents at C_1 in sugars are more easily removed under electron impact conditions because it generates a stabilized carbocation. This indicates that the two minor products are **21b** and **22b**, while the major one is **23b** (Scheme 5).

Problem of Regio- and Stereoselectivity. In all substrates and with all rhodium catalysts tested,

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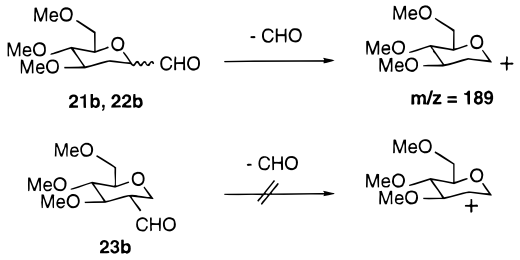
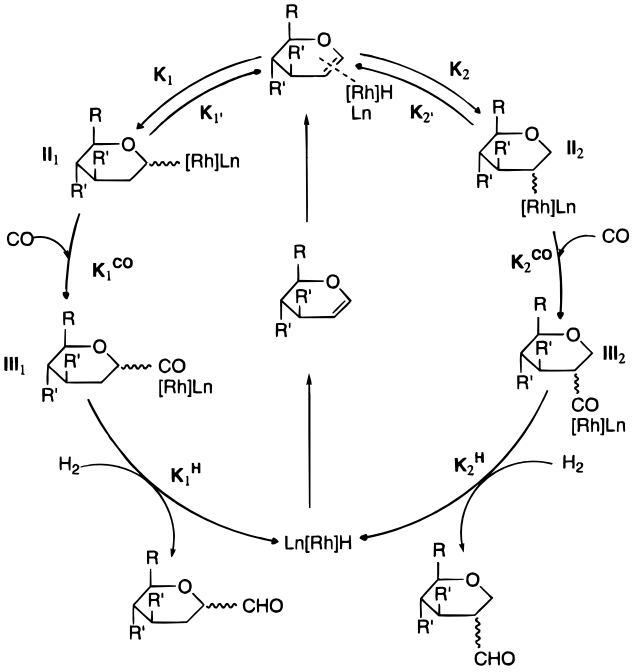
Scheme 5



Scheme 6



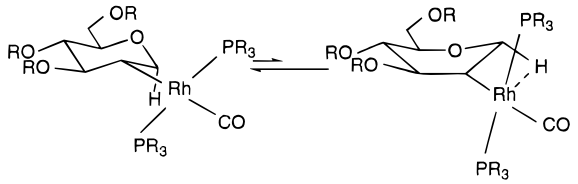
1 R = CH_2OR'', R'= OR'', R''= Ac
9 R = R' = H
20a R = CH_2OR'', R'= OR'', R''= Bn
20b R = CH_2OR'', R'= OR'', R''= Me

2-formylcarbohydrates were the main derivatives obtained when hydroformylating glucal derivatives, which is in contrast to the regioselectivity observed when cobalt catalysts were used[5] and to the results obtained when hydroformylating the closely related 3,4-dihydro-2*H*-pyran and 2,3-dihydrofuran, which gave mainly 1-formyl[9] derivatives.

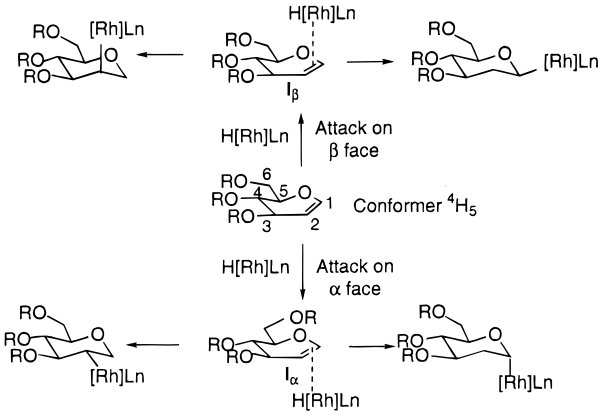
In a previous paper,[9] we showed that the regioselectivity in the hydroformylation of dihydrofuran and dihydropyran derivatives depended on the polarization of the double bond, the relative stability of the alkyl−metal complexes, the tendency to isomerize (i.e., the rate of β-elimination), and the ratio between the rates of formation of the acyl−metal intermediates.

We believe that for compound **9** (Scheme 6, R = R′= H), the alkyl−metal complex $\mathbf{II}_2$ was principally obtained because the new metal−carbon bond was formed at the carbon with the highest electron density.[9,13] However, because the C_1−metal bond in $\mathbf{II}_1$ is more polarized than the C_2−metal bond in $\mathbf{II}_2$, $\mathbf{III}_1$ forms from $\mathbf{II}_1$ faster than $\mathbf{III}_2$ from $\mathbf{II}_2$ ($K_1^{CO} > K_2^{CO}$). In this context, the reason the hydroformylation of 3,4-dihydro-2*H*-pyran principally gives the 1-formyl derivative must

Scheme 7



Scheme 8



be because of the fast isomerization process from $\mathbf{II}_2$ to $\mathbf{II}_1$ analogues and the faster formation of $\mathbf{III}_1$ species.

This isomerization process depends on two different factors: the high temperature required to perform the hydroformylation reaction (∼100 °C) and the auxiliary ligand used. The auxiliary ligand can increase or decrease the rate of β-elimination. This may be due to the size of the phosphite which reduces the number of ligands coordinated to the metal, thus creating the vacant site necessary for the β-elimination.

The results obtained with the glucal derivatives in the same conditions than for compound **9** confirm that the $\mathbf{II}_2$ alkyl−metal species are principally formed and that there is no β-elimination. This may be due to the demands of the β-elimination mechanism, which needs a "synperiplanar" arrangement of the metal and the β-hydride. Therefore, there must be a conformational change in the molecule, which is more difficult in substituted rings such as glucals than in nonsubstituted rings such as dihydropyran (Scheme 7).

The results of hydroformylating glucals using cobalt catalysts show that the isomerization process is also fast in this case. This may be because of the very high reaction temperature (∼200 °C) needed and the shorter cobalt−carbon bond which makes cobalt derivatives more sensitive to steric hindrance.

On the other hand, glucals are chiral compounds and the coordination of the double bond to the metal can give two different adducts, $\mathbf{I}_\alpha$ and $\mathbf{I}_\beta$ (Scheme 8). Glucal derivatives mainly have a $^4H_5$ conformation[17] although the conformers $^4H_5$ and $^5H_4$ may undergo a process of equilibrium at the reaction temperature, which would mean that the setereoselectivity is poor. However, the results show that the hydroformylation reaction of glucals is stereoselective and that the main product obtained is the result of the attack from the α face (adduct $\mathbf{I}_\alpha$) of the glucal. Moreover, the stereoselectivity is much better when the formyl group is in C_2 than when it is in C_1.

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The 1,2 addition of palladium complex and nucleophiles to glycals has been extensively studied by Doyle-Daves and colleagues.[18,19] When the starting material was 3,4,6-tri-*O*-acetyl-D-glucal **1** the main product obtained was also the result of the attack on the α face at C_2. In general, the stereoselectivity observed means that the palladium attacks the face which is opposite to the substituent at position 3. The fact that the stereoselectivity is high is due to stereoelectronic effects with a π_{ox}---$\pi^*_{C=C}$---σ^*_{3-OR} (vinylogous effect) interaction, which force the substituent at position 3 to adopt a pseudoaxial arrangement.[18]

The stereoselectivity in the hydroformylation of glucals with a rhodium catalyst, although smaller than in the reaction with palladium, can be explained in a similar way. There are practically no products with the 2-formyl axial group (*manno* configuration) because of the instability of the axial σ-alkyl-metal intermediate, which strongly interacts with the substituent at position 3 and with other substituents in the ring.

In conclusion, the catalytic system $[Rh_2(\mu\text{-OMe})_2(COD)_2]$/P(O-*o*-^{t}BuC$_6H_4$)$_3$ hydroformylates glucal derivatives in good yields and selectivities. The stereochemistry of the substituent at position C_3 of the glucal seems to be responsible for controlling the stereoselectivity of the reaction. The regioselectivity depends mainly on the polarization of the olefin and on the difficulty of producing the β-elimination process in conformationally rigid substrates.

Isolation and Characterization of Rhodium Species at the End of the Catalytic Reaction. When the catalytic systems **8**/P(O-*o*-^{t}BuC$_6$H$_4$)$_3$ and **19**/P(O-*o*-^{t}BuC$_6$H$_4$)$_3$ are used as the hydroformylation catalyst, the mononuclear species *trans*-[RhCl(CO)(P(O-*o*-^{t}BuC$_6$H$_4$)$_3$)$_2$][9] (**18**) can be isolated at the end of the catalytic reaction. The evaporation of the solvent and the extraction with methanol of the reaction products lead to the isolation of this species as a pale yellow crystalline solid which was characterized by elemental microanalysis, IR spectroscopy, and ^{31}P and ^{1}H NMR.

The ^{31}P{^{1}H} NMR spectrum shows only one doublet centered at 112.0 ppm, attributed to the two equivalent phosphorus atoms, with a relative trans conformation. The high coupling constant (J_{P-Rh} = 213 Hz) is in the range reported for analogous rhodium complexes *trans*-[RhCl(CO)(P(OR)$_3$)$_2$] (R = Me, J_{P-Rh} = 195.0 Hz; R = Ph, J_{P-Rh} = 217.4 Hz).[20]

In the carbonyl region, the infrared spectrum shows one ν(CO) frequency at 2012.5 cm^{-1} (s) in dichloromethane solution and at 2002.5 cm^{-1} in the solid state of the isolated product, according to the trans geometry of complex **18**. These values for ν(CO) frequences are in the range for other analogous rhodium complexes reported.[20]

Previous mechanistic studies by van Leeuwen et al.[21,22] on the use of [Rh]/P(O-*o*-^{t}BuC$_6$H$_4$)$_3$ systems have shown the presence of RhH(CO)$_3$P species, P = tris-*ortho*-*tert*-butylphenyl phosphite, under hydroformylation conditions. In our work the complex **18** was isolated at the end of the hydroformylation reaction. The presence of only one phosphite coordinated to the rhodium center in RhH(CO)$_3$P(O-*o*-^{t}BuC$_6$H$_4$)$_3$[21,22] is attributed to the large cone angle of the tris-*ortho*-*tert*-butylphenyl phosphite (175°).[14] This behavior is different from triphenylphosphine rhodium systems in which RhH(CO)$_2$(PPh$_3$)$_2$ is considered to be the main species during the hydroformylation reaction, in rapid equilibrium via CO and PPh$_3$ dissociation steps with other related species.[23,24]

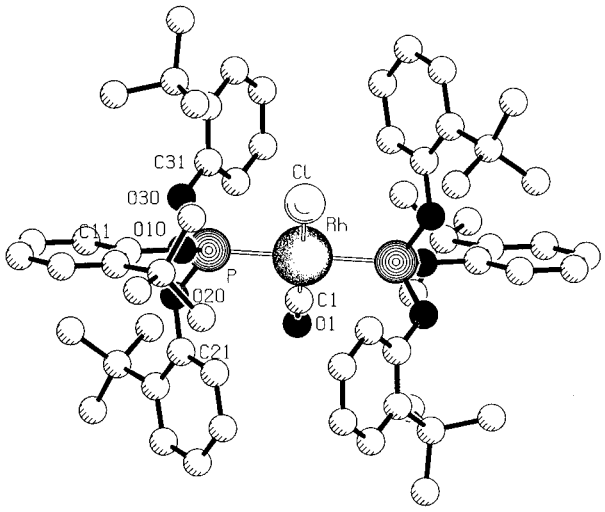

Figure 2. Molecular structure of the complex *trans*-[RhCl(CO)(P(O-*o*-^{t}BuC$_6$H$_4$)$_3$)$_2$] (**18**).

The isolation of *trans*-[RhCl(CO)(P(O-*o*-^{t}BuC$_6$H$_4$)$_3$)$_2$] shows the cleavage of the dinuclear $[Rh_2(\mu\text{-S(CH}_2)_3\text{NMe}_2)(COD)_2]$ and $[Rh(\mu\text{-OMe})(COD)]_2$ complexes, and the exchange of the hydride in the [RhH(CO)(PR$_3$)$_2$] species with chloride in the solvent.

X-ray Structure of *trans*-[RhCl(CO)(P(O-*o*-^{t}BuC$_6$H$_4$)$_3$)$_2$] (18). To confirm the characterization of *trans*-[RhCl(CO)(P(O-*o*-^{t}BuC$_6$H$_4$)$_3$)$_2$], we carried out a separate synthesis using $[Rh(\mu\text{-Cl})(COD)]_2$ as starting material, using a methodology previously described for related compounds,[25] and we obtained a crystal suitable for an X-ray structure determination. It should be noted that although several complexes with a *trans*-[RhCl(CO)(P(OR)$_3$)$_2$] molecular structure have previously been synthesized (R = Me,[20] Ph,[20,26,27] *p*-MePh,[27] *p*-ClPh[27]), none of these compounds has yet been structurally determined by X-ray diffraction, although X-ray structures of related phosphine complexes have been extensively reported.

The structure of *trans*-[RhCl(CO)(P(O-*o*-^{t}BuC$_6$H$_4$)$_3$)$_2$] consists of discrete mononuclear units in which the geometry at rhodium is square planar (Figure 2). The rhodium is placed on a crystallographic inversion center, and a CO/Cl structural disorder is present. The presence of CO was unequivocally determined by IR spec-

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Table 5. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Derivations in Parentheses for 18

Rh−Cl	2.370 (3)	P−O(20)	1.600(2)
Rh−C(1)	1.797 (6)	P−O(30)	1.603(2)
Rh−P	2.2856 (7)	O(10)−C(11)	1.384(2)
C(1)−O(1)	1.145(7)	O(20)−C(21)	1.378(2)
P−O(10)	1.592 (2)	O(30)−C(31)	1.369(3)
C(1)−Rh−P	89.7 (4)	O(30)−P−Rh	117.76 (8)
Cl−Rh−P	90.70 (8)	O(10)−P−O(20)	104.11 (11)
O(10)−P−Rh	114.49 (7)	O(10)−P−O(30)	101.54 (11)
O(20)−P−Rh	118.65 (8)	O(20)−P−O(30)	97.51 (8)

troscopy. Table 5 shows the most significant intramolecular distances and bond angles with their standard deviations.

The bond lengths and angles are similar to those reported previously for *trans*-[Rh(Cl)(CO)](PPh$_3$)$_2$][28] and *trans*-[Rh(Cl)(CO)](P^{t}Bu$_3$)$_2$].[29] The Rh−P distance (2.287(2) Å) for **18** is slightly shorter than the related Rh−P distance in the case of *trans*-[Rh(Cl)(CO)](PPh$_3$)$_2$],[28] average (2.323(6) Å).

Experimental Section

General Comments. All syntheses of rhodium complexes were performed using standard Schlenk techniques under a nitrogen atmosphere. Solvents were dried by standard methods and distilled under nitrogen immediately prior to use. The starting materials [{Rh(μ-Cl)(COD)}$_2$],[30] [{Rh(μ-OMe)(COD)}$_2$],[31] and P(O-*o*-^{t}BuC$_6$H$_4$)$_3$[11] were prepared according to reported methods. RhCl$_3$·*x*H$_2$O and phosphorus reactants were commercial samples and were used without further purification. Infrared spectra (range 4000−400 cm^{-1}) were recorded on a Nicolet 5ZDX-FT spectrophotometer in CH$_2$Cl$_2$ solutions or in KBr pellets. Elemental analyses were carried out on a Carlo-Erba microanalyzer, and fast atom bombardment mass spectra were obtained on a VG Autospect in a 3-nitrobenzyl alcohol matrix. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 spectrophotometer and chemical shifts are quoted in ppm downfield from internal TMS. ^{31}P NMR spectra were obtained on the same instrument at 120 MHz, using external 85% H$_3$PO$_4$ as reference. Mass spectrometry was performed on a Hewlett-Packard CG/MS 5988A spectrometer, using an Ultra-2 (diphenylsilicone 5%, dimethylsilicone 95%) 25 m × 0.2 mm column. Gas chromatography was performed on a Hewlett-Packard 5890 II chromatograph equipped with the column mentioned above. Flash chromatography was performed on silica gel 60 A CC. Solvents for chromatography were distilled at atmospheric pressure prior to use.

Catalysis. High-pressure hydroformylation experiments (50−75 bar) were carried out in a Berghof autoclave, and were magnetically stirred and electrically heated. These experiments were not performed at constant pressure, but for the amount of substrate used the pressure drop was never more than 3 bar.

General Procedure. In a standard experiment, a solution of the substrate (5 mmol), the catalyst (0.05 mmol), and the phophorous cocatalyst (0.5 mmol) in 15 mL of the solvent was placed in the evacuated autoclave and heated while stirring. Once the system reached thermal equilibrium the gas mixture was introduced to reach the working pressure. Small samples of the catalytic solution were taken at intervals for analysis. After each run, the system was allowed to cool and the gas vented. The reaction mixture was removed from the autoclave and immediately analyzed by FT-IR spectroscopy to determine the metal carbonyl species and by gas chromatography and ^{1}H NMR spectroscopy to determine the conversion and the selectivity of the reaction.

Hydroformylation of 3,4,6-Tri-*O*-acetyl-D-glucal. 3,4,6-Tri-*O*-acetyl-D-glucal was hydroformylated following the general procedure. The resulting reaction mixture was evaporated to dryness and purified by flash chromatography (ethyl acetate/hexane 2:1) so obtaining the pure compounds **14**, **15**, and **17**. Pure compound **16** was recovered as its 2,4-dinitrophenylhydrazone derivative.

4,6-Di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-2-*C*-formyl-D-2-enerythritol (14). ^{1}H NMR (CDCl$_3$): δ 2.12 (s, 3H, OCOCH$_3$), 2.14 (s, 3H, OCOCH$_3$), 3.70 (ddd, J = 8.4, 5.4, 2.7, 1H, H$_5$), 4.21 (dd, J = 12, 5.4, 1H, H$_6$), 4.29 (dd, J = 12, 2.7, 1H, H$_{6'}$), 4.35 (ddd, J = 17, 2.7, 2.7 1H, H$_{1a}$), 4.58 (ddd, J = 17, 2.2, 2.2, 1H, H$_{1e}$), 5.50 (dq, J = 8.4, 2.7, 2.7, 2.2, 1H, H$_4$), 6.72 (ddd, J = 2.7, 2.7, 2.2, 1H, H$_3$), 9.50 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$): δ 20.6, 20.7, 62.8, 63.4, 65.2, 73.9, 141.6, 142.5, 169.9, 170.6, 190.6. Anal. Found: C, 53.52; H, 5.06. Calcd: C, 53.77; H, 5.39.

3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-deoxy-2-*C*-formyl-D-glucitol (15). ^{1}H NMR (CDCl$_3$): δ 1.98 (s, 3H, OCOCH$_3$), 1.99 (s, 3H, OCOCH$_3$), 2.11 (s, 3H, OCOCH$_3$), 2.99 (ddt, J = 17, 17, 8, 2.7, 1H, H$_2$), 3.40−3.60 (m, 1H, H$_{1a}$), 4.00−4.25 (m, 4H, H$_{1e}$, H$_5$, H$_6$, H$_{6'}$), 4.95 (dd, J = 14, 11, 1H, H$_4$), 5.22 (dd, J = 17, 14, 1H, H$_3$), 9.54 (d, J = 2.7, 1H, CHO). ^{13}C NMR (CDCl$_3$): δ 20.6, 20.7, 53.8, 62.3, 64.8, 68.3, 70.8, 78.9, 169.7, 170.1, 171.0, 197.2.

4,6-Di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-2-*C*-formyl-D-arabinitol (16) (as 2,4-Dinitrophenylhydrazone Derivative). To a solution of the mixture of hydroformylated compounds and acetic acid (three drops) in ethanol was added dropwise a saturated solution of 2,4-dinitrophenylhydrazine in ethanol until no color change was observed. When the reaction had finished, water was added until it became turbid and the solution was first left at room temperature and then cooled to 5 °C. The solid formed was filtered off and vacuum-dried. The mixture of hydrazone obtained was purified by TLC (ethyl acetate/hexane 1:1) and the pure compound **16** was recovered as its 2,4-dinitrophenylhydrazone derivative. ^{1}H NMR (CDCl$_3$): δ 1.16 (ddd, J = 11, 10.3, 5.4, 1H, H$_{3a}$), 2.00 (s, 3H, OCOCH$_3$), 2.07 (s, 3H, OCOCH$_3$), 2.72 (dd, J = 11, 4.4, 1H, H$_{3e}$), 2.91 (td, J = 5.4, 3.3, 3.3, 1H, H$_2$), 3.59 (dt, J = 10, 5.3, 5.3, 1H, H$_5$), 3.79 (dd, J = 12, 3.3, 1H, H$_{1a}$), 4.10 (d, J = 12, 1H, H$_{1e}$), 4.10 (d, J = 5.3, 2H, H$_6$, H$_{6'}$), 5.12 (ddd, J = 10.3, 10, 4.4, 1H, H$_4$), 7.57 (d, J = 3.3, 1H, CH=), 8.20−9.10 (m, 5H, Ar), 11.12 (bs, 1H, NH).

3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-hexoarabinitol (17). ^{1}H NMR (CDCl$_3$), δ 1.82 (dq, J = 12.5, 12.5, 12.5, 5, 1H, H$_{2a}$), 2.03 (s, 3H, OCOCH$_3$), 2.04 (s, 3H, OCOCH$_3$), 2.07 (d, J = 12.5, 1H, H$_{2e}$), 2.09 (s, 3H, OCOCH$_3$), 3.44−3.48 (m, 2H, H$_{1a}$, H$_{1e}$), 4.05 (ddd, J = 11.5, 5, 2, 1H, H$_5$), 4.10 (dd, J = 12.5, 2, 1H, H$_{6'}$), 4.23 (dd, J = 12.5, 5, 1H, H$_6$), 4.94−5.00 (m, 2H, H$_3$, H$_4$). ^{13}C NMR (CDCl$_3$): δ 20.9, 21.0, 21.1, 31.2, 63.6, 65.7, 69.5, 72.6, 76.8, 170.5, 171.1, 171.5.

Hydroformylation of Tri-*O*-benzyl-D-glucal. 4,5,7-Tri-*O*-benzyl-2,6-anhydro-D-glucoheptopyranose (22a). ^{1}H NMR (CDCl$_3$): δ 1.54 (dt, J = 12.5, 12.5, 11.5, 1H, H$_{2a}$), 2.42 (td, J = 12.5, 5, 2.5, 1H, H$_{2e}$), 3.83 (dd, J = 12.5, 2.5, 1H, H$_1$), 3.60−4.00 (m, 3H, H$_5$, H$_6$, H$_{6'}$), 4.60−4.80 (m, 8H, CH$_2$Ph, H$_3$, H$_4$), 7.10−7.60 (m, 15H, Ph), 9.70 (s, 1H, CHO). ^{13}C NMR (CDCl$_3$), δ 31.4, 69.2, 71.4, 73.4, 73.5, 75.1, 79.1, 79.4, 80.2, 127.0−128.7, 137.0−139.0, 201.2.

3,4,6-Tri-*O*-benzyl-1,5-anhydro-2-deoxy-2-*C*-formyl-D-glucitol (23a) (as 2,4-Dinitrophenylhydrazone Derivative, see Methodology for Derivatization of 16). ^{1}H NMR (CDCl$_3$), δ 2.85 (ddd, J = 10.5, 10.3, 5.3, 1H, H$_2$), 3.44 (dd, J = 11, 10.5, 1H, H$_{1a}$), 3.45 (m, 2H, H$_4$, H$_5$), 3.66 (t, J = 10.3,

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1H, H_3), 3.72 (m, 2H, H_6, $H_{6'}$), 4.08 (dd, J = 11, 5.3, 1H, H_{1e}), 4.50−4.90 (m, 6H, CH_2Ph), 6.85 (d, J = 5.3, 1H, CH═N), 7.10−9.10 (m, 15H, Ph), 10.60 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ 45.9, 67.7, 68.7, 75.5, 74.8, 75.1, 79.3, 79.7, 82.1, 116.5, 123.5, 127.7, 128.7, 129.0, 130.1, 137.8, 137.9, 138.0, 138.1, 144.7, 148.7.

Preparation of [RhCl(CO)(P(O-*o*-^{t}BuC$_6$H$_4$)$_3$)$_2$] (18). A stream of CO was bubbled through a solution of [Rh$_2$(μ-Cl)$_2$(cod)$_2$] (40 mg, 0.1 mmol) in dichloromethane (5 mL) and then tris-(*o*-*tert*-buylphenyl)phosphite (95.6 mg, 0.2 mmol) was added. A brisk gas evolution and a change in color to pale yellow were observed. After 30 min, the solution was concentrated and ethanol was added and a yellow crystalline solid precipitated, which was filtered off, washed with cold ethanol, and vacuum-dried to give a yellow crystalline compound. Yield 85% (133.4 mg). Elemental analysis: Found: C, 65.2; H, 6.9. Calcd for $C_{61}H_{78}O_7P_2ClRh$: C, 65.6; H, 7.1. IR (ν(CO) cm^{-1}) in CH_2Cl_2 solution, 2012.5; in KBr, 2002.5. ^1H NMR ($CDCl_3$): δ 1.40(s, 54H, CH_3), 6.89 (t, J = 8.2, 8.1 Hz, 6H, Ar), 6.96 (t, J = 8.2, 8.1 Hz, 6H, Ar), 7.31 (d, J = 8.1 Hz, 6H, Ar), 7.70 (d, J = 8.1 Hz, 6H, Ar). ^{13}C NMR ($CDCl_3$): δ 30.3, 35.0, 120.6, 123.9, 126.6, 127.3, 139.2, 150.4. ^{31}P NMR: δ 112.0 (d, J_{P-Rh} = 213 Hz).

Crystal Structure Determination of 18. A suitable yellow single crystal of **18** was obtained by slow evaporation from a CH_2Cl_2/EtOH solution. The crystal was mounted in an Enraf-Nonius CAD4 automatic diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69). Crystallographic and experimental details are summarized in Table 6. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects. Empirical absorption correction[32] from ψ-scans was applied. The structure was solved by direct methods (SHELXS86)[33] and refined by least squares on F^2 for all reflections (SHELXL93[34]). The asymmetric unit is half a molecule, the rhodium is placed in a crystallographic inversion center. On the basis of chemical and spectroscopic grounds, the rhodium is bonded to a carbonyl group and a chlorine atom, so the complex is not centrosymmetric and the chlorine and the CO group show positional disorder. The refinement was carried out using a restrained geometry affecting the Cl−Rh−CO moiety (d_{Rh-C1} = 1.85(1), d_{Rh-O1} = 3.00(1), d_{C1-O1} = 1.15(1)). All non-H atoms were refined anisotropically, and the H-atoms were refined using a riding model with thermal parameters fixed at 1.5 (methyl H) or 1.2 (the rest) times the U_{iso} of the corresponding carbon atoms.

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Table 6. Crystal Data and X-ray Experimental Details for 18

empirical formula	$C_{61}H_{78}ClO_7P_2Rh$
fw	1123.53
wavelength	0.71069 Å
crystal system	monoclinic
space group	*C*2/*c*
unit cell dimensions	a = 12.150(3) Å
	b = 24.457(2) Å
	c = 20.045(5) Å
	α = 90°
	β = 96.80(2)°
	γ = 90°
volume	5914(2) Å^3
Z	4
density (calcd)	1.262 Mg/m^3
abs coeff	0.437 mm^{-1}
F(000)	2368
crystal size	0.5 × 0.4 × 0.2 mm
θ range for data collection	1.67−24.97°
index ranges	$-14 \le h \le 14$
	$0 \le k \le 28$
	$0 \le l \le 23$
no. of indep reflcns	5202
no. of obsd reflcns	3936
refinement method	full-matrix least-squares on F^2
data/restraints/params	5202/39/304
goodness-of-fit on F^2	1.107
final R indices[a] ($F > 4\sigma(F)$)	$R(F)$ = 0.039
	$Rw(F^2)$ = 0.115
final R indices (all data)	$R(F)$ = 0.057
	$Rw(F^2)$ = 0.118
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.075P)^2$, where $P = (F_o^2 + 2F_c^2)/3$
largest diff peak and hole	0.39 and −0.43 e/Å^3

[a] $R(F) = \sum||F_o| - |F_c||\sum/F_o|$; $Rw(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

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Supporting Information Available: ORTEP diagram of the molecular structure with full numbering scheme and tables of the atomic coordinates of heavy atoms and bond distances and angles for [RhCl(CO)(P(O-*o*-^{t}BuC$_6$H$_4$)$_3$)$_2$] are available (13 pages). Ordering information is given on any current masthead page.

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