Rhodium N-Heterocyclic Carbene Carboxylato Complexes: Synthesis, Structure Determination, and Catalytic Activity in the Hydroformylation of Alkenes

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Rhodium carboxylato complexes bearing N-heterocyclic carbene ligands, $[Rh(IPr)(CO)_2(OAc)]$ (**1**) and $[Rh(IPr)_2(CO)(OAc)]$ (**2**), have been synthesized and characterized. The two complexes are catalytically active for the regioselective hydroformylation of both aryl and aliphatic alkenes with regioselectivities of up to 40:1, without concomitant isomerization or hydrogenation.

Introduction

The hydroformylation of alkenes is a well-known and industrially important catalytic reaction.[1] First discovered by Roelen in 1938, the reaction has since become the largest volume industrial process involving homogeneous catalysts, with production levels on the order of several million tons annually.[2] Depending on the type of substrate employed, alternate regioisomers are preferred. For example, high linear selectivity is desirable in the hydroformylation of propene, since only *n*-butanal can be used in the preparation of a variety of high-volume commodity chemicals, including paint solvents and plasticizers.[3]

Conversely, in the case of vinylarenes, the branched products are more desirable, since oxidation generates the corresponding 2-arylpropionic acids, which are an important class of analgesic drugs, including ibuprofen and naproxen. Although the active form of most profen drugs is the *S* enantiomer, the largest volume of these (ibuprofen/Advil) is sold as the racemate, since the inactive *R* form is converted into the *S* enantiomer in the body.[4,5] Therefore, stereocontrol is important in some cases; however, achieving high regioselectivity is essential in the hydroformylation of all alkenes.

Typical catalytic systems using rhodium, including a large portion of industrial processes, employ high concentrations of phosphine ligands to stabilize the metal center and control regioselectivity.[6] In the case of propene hydroformylation, the requirement for such high concentrations of phosphine is related to the lability of the Rh−P bond, especially in the presence of CO, and the higher selectivities obtained with catalysts bearing more than one phosphine.[7−9] Recently, metal complexes containing N-heterocyclic carbenes (NHCs), have provided air- and moisture-stable catalysts for a variety of reactions. The steric bulk of the more popular 1,3-diarylimidazol-2-ylidene ligands IMes and IPr and the generally decreased lability of their bonds to metals[10−13] (although see refs 14 and 15) were our initial motivations to study these complexes as hydroformylation catalysts.

Our group,[16,17] in addition to the groups of Coleman,[18] Weberskirch,[19] Nuygen/Buchmeiser,[20] Herrmann,[21] and Peris/Fernandez,[22] has reported the synthesis of various Rh−NHC modified hydroformylation catalysts. In the case of vinylarenes, high regioselectivities (up to 97% of the branched) have been attained along with high yields.[16,17,22] The most active catalysts for the hydroformylation of terminal aliphatic olefins such as 1-octene have been described by Weberskirch,[19] displaying turnover (TO) frequencies of up to 3500 TO/h. Unfortunately, this and other catalyst systems[18,20,23,26] all promote isomerization

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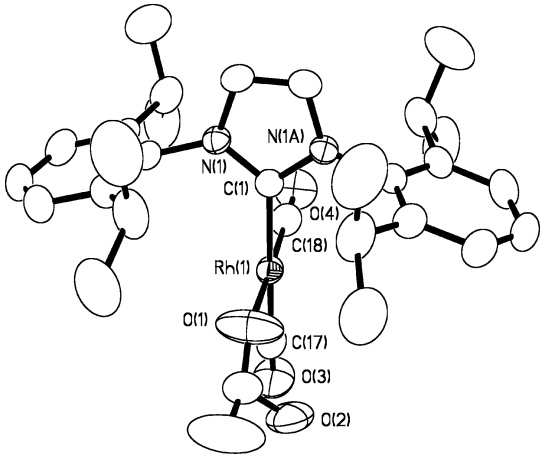

Figure 1. Crystallographically determined structure of **1**, displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms have been removed for clarity. Selected interatomic distances (Å) and angles (deg): Rh−C(1), 2.070(3); Rh−C(18), 1.813(4); C(18)−O(4), 1.151(4); Rh−C(17), 1.917(3); C(17)−O(3), 1.132(4); Rh−O(1), 2.043(3); O(1)−Rh−C(1), 86.95(11); O(1)−Rh−C(17), 93.66(15); O(1)−Rh−C(18), 176.60(12); C(18)−Rh−C(17), 89.75-(15); C(1)−Rh−C(18), 86.95(12); C(1)−Rh−C(17), 176.70(13).

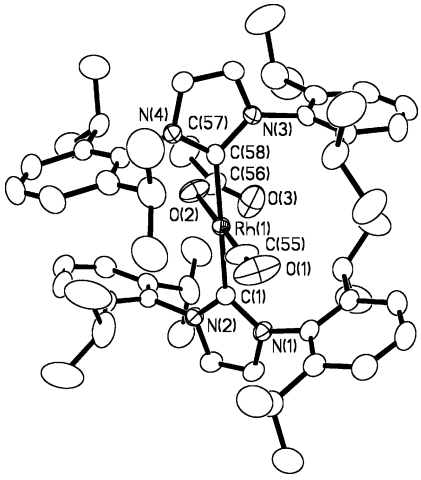

Figure 2. Crystallographically determined structure of **2**, displaying thermal ellipsoids drawn at the 50% confidence level. Hydrogen atoms have been removed for clarity. Selected interatomic distances (Å) and angles (deg): Rh−C(55), 1.789(3); Rh−C(58), 2.068(2); Rh−O(2), 2.07808(18); Rh−C(1), 2.078(2); C(55)−O(1), 1.151(3); C(55)−Rh−C(58), 87.94(10); C(55)−Rh−O(2), 174.04(10); C(58)−Rh−O(2), 87.01(8); C(55)−Rh−C(1), 91.58(10); C(58)−Rh−C(1), 179.14(8); O(2)−Rh−C(1), 93.43.

of the olefin on a time scale similar with that of hydroformylation. The result is moderate linear selectivities for the linear isomer early in the reaction (ca. 2.5:1) which are degraded to less than 1:1 upon completion of the reaction.

The group of Weberskirch reported the catalytic activity of Rh−NHC complexes that are immobilized on amphiphilic block copolymers for the aqueous biphasic hydroformylation of 1-octene.[23] Increased activity was observed upon reuse, a fact the authors attributed to the generation of the catalytically active hydride from bromide precatalyst. Although their activity in the hydroformylation reaction has not been reported, Rh hydrido carbonyl species containing NHCs as ancillary ligands have been described by Whittlesey et al.[24]

Cobalt−NHC complexes have also been examined in the hydroformylation of alkenes. Interestingly, the dimer $[Co(CO)_3(IMes)]_2$ showed no activity,[25] while the related hydride $HCo(CO)_3(IMes)$ was catalytically active, although with modest turnover frequencies, for the hydroformylation of 1-octene. Again, isomerization of the olefin was observed.[26]

Herein we report the synthesis and reactivity of mono- and bis(carbene) complexes of Rh which are catalytically active for the hydroformylation of a variety of olefins. These complexes represent the first example of N-heterocyclic carbene complexes that catalyze the hydroformylation of 1-alkenes without concomitant isomerization. They also are the first examples of square-planar catalytically active rhodium carboxylato complexes bearing N-heterocyclic carbene ligands.

Results and Discussion

Complex **1** (Figure 1) was prepared by treating the previously reported rhodium dimer $[Rh(OAc)(CO)_2]_2$[27] with 2 equiv of IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) in THF, affording a red mixture, which turned yellow within minutes. Filtration over a bed of Celite under aerobic conditions gave **1** as an air-stable complex in 72% yield, respectively. In order to prepare the bis(carbene) complex **2** in reasonable yield, 3 equiv of IPr was required per rhodium. Unfortunately, under these conditions, large amounts of carbene byproducts complicated the purification of **2**. With less than 3 equiv of IPr, **2** was contaminated with **1**, which was not able to be separated on a bulk scale. However, X-ray-quality crystals of **2** could be obtained by crystallization from THF and hexanes. As **2** proved to be essentially inactive in the hydroformylation of alkenes,[28] its synthesis was not optimized further. The structures of $[Rh(IPr)(CO)_2(OAc)]$ (**1**) and $[Rh(IPr)_2(CO)(OAc)]$ (**2**) are shown in Figures 1 and 2, respectively, and crystallographic parameters are given in Table 1.

The crystal structures of the two complexes reveal that they are both pseudo square planar, with the acetato ligands bound to the metal center in a unidentate manner. The X-ray structure of **1** (Figure 1) shows that the CO ligands are oriented cis to one another, which was confirmed in the bulk material by $^{13}C\{^1H\}$ NMR and IR spectroscopy. The $^{13}C\{^1H\}$ NMR displayed two carbonyl resonances at 187.1 and 185.8 ppm, and in the IR, two CO stretches at 2070 and 1990 cm^{-1} were observed. The IR data for **1** are similar to those recently reported by Herrmann and co-workers for analogous structures.[29] The trans geometry of **2** seen in the crystal structure of this compound (Figure 2) was also confirmed in solution by $^{13}C\{^1H\}$ NMR, which featured only one carbene (190.6 ppm) and one carbonyl resonance (191.8 ppm). The IR spectrum contained only one CO stretch at 1952 cm^{-1}, consistent with the presence of only one CO ligand. Notably, the ν(CO) value is at a lower wavenumber than for the previously reported phosphine derivative,[30] indicative of a more electron-rich metal center and comparable to the case for a previously reported bis-NHC rhodium−CO complex, $[Rh(IMe_2)(CO)Cl]$.[29,31,32] In addition, the Rh−carbon (IPr) bond lengths of **1** and **2** are in the

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(28) Complex **2**, prepared with only 2 equiv of IPr, gave turnover frequencies that were 2 orders of magnitude lower than for the mono(carbene) complex **1**. Considering that the more active complex **1** was present as a contaminant, it is entirely possible that even the low activity observed with **2** can be attributed to complex **1**.

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Table 1. Crystallographic Data for Compounds 1 and 2

	1	2
formula	$C_{31}H_{39}N_2O_4Rh$	$C_{57}H_{75}N_4O_3Rh$
fw	606.55	967.12
color/habit	yellow/ block-shaped	yellow/ block-shaped
cryst dimens (mm^3)	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.08
cryst syst	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/n$
a (Å)	9.5386(8)	12.4289(8)
b (Å)	17.4011(15)	21.2152(14)
c (Å)	9.7950(9)	19.9599(13)
β (deg)	111.0870(10)	93.3450(10
V (Å^3)	1516.9(2)	5254.1(6)
Z	2	4
T (K)	180(2)	180(2)
D_{calcd} (g cm^{-3})	1.328	1.223
μ (mm^{-1})	0.599	0.371
F(000)	632	2056
θ range (deg)	2.29−25.00	1.40−25.00
index ranges (h, k, l)	±11, ±19, ±11	±14, ±25, ±23
no. of rflns collected	8984	30 696
no. of indep rflns/R_{int}	2765/0.0209	9249/0.0270
no. of data/restraints/ params	2765/8/264	9249/0/846
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0277/0.0716	0.0314/0.0832
R1/wR2 (all data)[a]	0.0299/0.0729	0.0438/0.0894
GOF (on F^2)[a]	1.000	1.000
largest diff peak/hole (e Å^{-3})	+0.558/−0.498	+0.903/−0.344

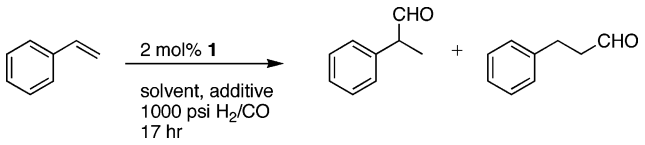
[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

commonly observed range, and the C−O bond lengths of the carbonyls cis and trans to the carbene of **1** are 1.151(4) and 1.132(4) Å, respectively. As would be expected due to the larger trans effect of the IPr ligand, the carbonyl in the trans position possesses a longer Rh−C bond and therefore a shorter C−O bond.

The hapticity of metal−carboxylato complexes can be spectroscopically probed by examining the difference between the $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ stretches (Δ), where it is believed that chelating ROCO groups have $\nu(OCO)_{asym}$ and $\nu(OCO)_{sym}$ very similar to those for the free ion.[33a] Unidentate ROCO groups, on the other hand, possess asymmetric stretches at higher frequencies and therefore larger Δ values than the free ions. The unidentate coordination of the acetate ligand observed crystallographically for both **1** and **2** is confirmed in the bulk material by the Δ values of 231 and 259 cm^{-1}, respectively (Table 2).

Given their similarity to catalytically active rhodium−NHC complexes previously reported by our group,[16,17] we investigated the ability of the two new complexes to hydroformylate common substrates. Initial studies by Wilkinson demonstrated that rhodium-catalyzed hydroformylations employing catalysts with M−X bonds exhibit an induction period, during which hydrogen halide is eliminated, generating the active hydrido−rhodium complex.[34] Nuyken, Buchmeiser, et al. have also documented 30−60 min induction periods in their study of an interesting class of tetrahydropyrimidin-2-ylidene-ligated complexes.[20] In Wilkinson's study, the induction period increases in the order Cl < Br < I;[35] however, Nuyken and Buchmeiser found no difference between chloride and bromide complexes with tetrahydropyrimidin-2-ylidene-ligated complexes.[20] Our previous work with IMes-type ligands suggested that HX elimination was an important contributor to catalytic activity, with turnover numbers increasing from ca. 10−30 to ca. 100−125 TO/h upon the addition of NEt_3 which is known to promote HX elimination.[16] Thus, we were interested in determining whether carboxylato ligands would produce the catalytically active species more readily. An optimization study was initially undertaken, in which solvents, temperature, and different additives were screened (Table 3).

Table 3. Optimization of the Hydroformylation of Styrene Using 1[a]



entry	solvent	temp (°C)	additive	yield (%)	B:L
1	MeCN	60	none	<1	n/a
2	DCM	60	none	47	10
3	hexanes	60	none	9	14
4	THF	60	none	<1	n/a
5	benzene	60	none	27	22
6	benzene	40	none	8	>40
7	benzene	80	none	93	10
8	benzene	80	NEt_3 (2%)	4	n/a
9	benzene	80	NEt_3 (20%)	16	5
10	benzene	80	KI (2%)	7	6
11	benzene	80	KI (20%)	11	3
12	benzene	80	PPh_3 (2%)	78	27
13	benzene	80	PPh_3 (20%)	44	20

[a] Conditions: 2 mol % catalyst loading in a 0.100 M solution of styrene for 17 h at various temperatures, under a 1000 psi (1:1) atmosphere of CO and H_2.

In the hydroformylation of styrene, complex **1** was shown to be a competent catalyst in a variety of solvents including dichloromethane and hexanes. However, the highest regioselectivity in favor of the branched isomer was observed in benzene, and so this solvent was chosen for further optimization studies.

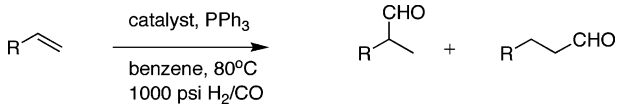
A number of different additives shown to be effective with previous hydroformylation catalysts were tested. In the absence of any additives, complex **1** gave the corresponding aldehydes in 93% yield after 16 h with a 10/1 selectivity in favor of the branched isomer (entry 7). Interestingly, with this catalyst precursor, triethylamine alone had a detrimental affect on activity. The reason for this deactivation is currently under investigation. In contrast to a related complex synthesized by Otto and co-workers,[36] complex **1** is catalytically active in the absence of additional phosphine. However, the addition of 1 equiv of triphenylphosphine did improve the selectivity to 27/1[35] with a slight decrease in yield to 78% (entry 12).[34] The addition of more than 1 equiv of PPh_3 did not lead to an improvement in yield or selectivity (compare entries 12 and 13 in Table 3).[37]

Examination of the progress of the reaction with high concentrations of substrate, 2.7 M, indicated that the turnover frequency of the catalyst was reasonably high: over 500 h^{-1},

Table 2. Selected IR Stretches of Compounds 1 and 2

entry	structure	ν(CO) (cm^{-1})	$\nu(OCO)_{asym}$ (cm^{-1})	$\nu(OCO)_{sym}$ (cm^{-1})	Δ (cm^{-1})
1	NaOAc[33b]	n/a	1578	1414	164
2	unidentate OCOR[33c]	n/a	1580−1650	1310−1390	210−270
3	chelate OCOR[33c]	n/a	1490−1540	1400−1470	40−120
4	**1**	2070, 1990	1613	1382	231
5	**2**	1952	1619	1360	259

Table 4. Hydroformylation of Aromatic and Aliphatic Olefins[a]



entry	substrate	TOF (h^{-1})[b]	B:L
1	styrene	338	21:1
2	4-chlorostyrene	515	23:1
3	4-methoxystyrene	334	9:1
4	4-methylstyrene	426	11:1
5	4-acetoxystyrene	282	15:1
6	4-phenyl-1-butene	725	1:2.3
7	1-decene	345	1:3

[a] Conditions: 0.05 mol % of **1**, 0.05 mol % of PPh_3 in a ca. 1.0−1.2 M benzene solution of substrate under a 1000 psi (1:1) atmosphere of CO and H_2. [b] TOF's determined after 1 h by ^1H NMR using an internal standard.

depending on the substrate (Table 4). We were therefore able to lower the catalyst loading to 0.05 mol % and still achieve reasonable yields for a number of vinylarenes.

The ability of complex **1** to hydroformylate aliphatic alkenes was also investigated using 4-phenyl-1-butene and 1-decene as substrates. As noted previously, the hydroformylation of aliphatic alkenes is plagued by isomerization of the double bond, believed to occur by elimination from the proposed rhodium alkyl intermediate, and competitive hydrogenation to the corresponding alkane.[7] The hydroformylation of 4-phenyl-1-butene provided an interesting indicator of the propensity for isomerization, as isomerization should lead to 2-phenylpentanal, because of the proposed high stability of the Rh−benzyl intermediate preceding the aldehyde product.[39] Hydroformylation of the internal olefin 2-octene was also carried out.

For 4-phenyl-1-butene, the branched and linear aldehydes were obtained with moderate selectivity favoring the linear isomer (2.3:1), without any detectable isomerization or hydrogenation (Table 4). Yields and TOF's were reasonably high: 96% and 725 h^{-1}, respectively. The branched to linear selectivity was determined to be the same at 1 h and at 19 h. This is significant, since isomerization of the olefin usually results in a degredation of linear to branched selectivity as the reaction proceeds. In the case of 1-decene, only the 1- and 2-aldehydes were detected, with no observable isomerization or hydrogenation of the double bond. In addition, the B/L ratio was the same after 1 or 19 h. In the case of 2-octene, although the reaction was quite slow,[40] less than 1% of the *n*-aldehyde was observed, which would have resulted from isomerization to the 1-alkene and hydroformylation. The high mass balance obtained (96%) implies that hydrogenation is also not an issue with this substrate.

Since high linear selectivity in the hydroformylation of aliphatic olefins is generally attributed to complexes which have more than one phosphine ligand,[7−9] bis(carbene) complex **2**, bearing two IPr ligands in a trans relationship, was examined in the hydroformylation of olefins. Low TOFs, on the order of 1−3 h^{-1}, were obtained using **2**. Although this may be due to the significant steric bulk possessed by the carbene ligands, it may also be the case that all the catalytic activity observed should be attributed to the presence of small amounts of complex **1** (vide supra). Since the lability of the carbene−metal bond has been documented in the case of Rh and other metals,[14,15,41−47] it is possible that the limited catalytic activity observed with **2** can actually be attributed to decomposition to a mono(carbene) species. These possibilities are currently under examination in our laboratory. The activity of complexes bearing less sterically hindered carbenes is also being investigated.

Conclusions

In conclusion, two new rhodium N-heterocyclic carbene complexes have been prepared, which represent the first examples of such complexes possessing unidentate carboxylato ligands. Complex **1** represents the most active NHC-modified rhodium hydroformylation catalyst reported to date for the hydroformylation of styrene derivatives. High regioselectivity, up to 40/1 in favor of the branched isomer, was observed in the hydroformylation of vinylarenes with **1**. Compound **1** shows good activity in the hydroformylation of terminal aliphatic olefins, with TOF's of up to 725 h^{-1} and turnover numbers as high as 1900. Most importantly, the reactions of these substrates occur without concomitant isomerization, which might be attributed to the steric bulk of the IPr ligand.

Experimental Section

General Considerations. Both the rhodium dimer $[Rh(CO)_2(OAc)]_2$[27] and the free carbene IPr[48] were prepared according to literature procedures. Benzene and triethylamine were purified under an argon atmosphere from calcium hydride. All other solvents (THF, CH_2Cl_2, hexanes, MeCN) were purified using an MBraun SPS solvent system. All solvents were purged of oxygen using a minimum of three freeze−pump−thaw cycles before being brought into the glovebox. All alkene substrates were purchased from commercial sources, distilled under vacuum via bulb-to-bulb distillation, deoxygenated using a minimum of three freeze−pump−thaw cycles, and stored in the glovebox at −20 °C. Triphenylphosphine was obtained from commercial sources and recrystallized

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(37) Otto et al.[36] noted that a Rh−NHC acac complex was catalytically inactive until the addition of excess PPh_3, which NMR studies indicated led to the generation of $HRh(CO)(PPh_3)_3$-type complexes. In our case, catalytic activity is actually decreased by the addition of PPh_3, although selectivity improves in the case of vinylarenes. In the case of decene, virutally identical results were obtained (with 1 equiv of PPh_3, B:L = 1.8:1, 91% yield; without PPh_3, B:L = 1.6:1, 73% conversion, 90% mass recovery, no 2-decene or decane dectected). Although we cannot rule out the generation of carbene-free Rh species at this point, the yields and selectivities obtained in this study do not match those reported for $Rh(CO)(acac)(PPh_3)/PPh_3$ mixtures as reported by Trzeciak et al.[38]

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from absolute ethanol prior to use. KI was recrystallized from boiling distilled water and dried under vacuum over P_2O_5. ^1H and $^{13}C\{^1H\}$ NMR spectra were performed using Bruker Avance 400 and 500 MHz spectrometers. Mass spectra were determined by TOF EI mass spectrometry on a Biosystems/MDS Sciex QSTAR XL Q-TOF mass spectrometer. Elemental analysis was performed by Canadian Microanalytical Systems Ltd. X-ray data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer.

Synthesis of Catalysts. (a) Preparation of [Rh(IPr)(CO)$_2$(OAc)] (1). An oven-dried round-bottomed flask containing a stirbar was brought into the glovebox, and in it was placed [Rh(CO)$_2$(OAc)]$_2$ (19.5 mg, 44.7 μmol), IPr (34.9 mg, 89.8 μmol), and 5 mL of THF. The reaction mixture was stirred for 2 h, after which time the solution had turned from red-orange to yellow. After 2 h the flask was removed from the glovebox and the reaction mixture filtered through a plug of Celite under aerobic conditions. The filtrate was concentrated in vacuo to give a fine yellow, air-stable powder. X-ray-quality crystals were obtained by slow diffusion of hexanes into a THF solution of the complex (yield 39.0 mg, 72%). Anal. Found (calcd) for $RhC_{31}H_{39}O_4N_2$: C, 61.62 (61.37); H, 6.63 (6.48); N, 4.56 (4.62). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.51 (t, 2H), 7.32 (d, 4H), 7.16 (s, 2H), 2.84 (septet, 4H), 1.85 (s, 3H), 1.32 (d, 12H), 1.12 (d, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 187.1 (d, J_{CRh} = 69 Hz, Rh−CO), 185.8 (d, J_{CRh} = 58 Hz, Rh−CO), 181.8 (d, J_{CRh} = 48 Hz, Rh−C_{IPr}), 176.3, 146. 2, 135.3, 130.7, 125.3, 124.1, 68.29, 28.8, 26.5, 22.9. IR (KBr, cm^{-1}): 2070, 1990, 1613, 1382.

(b) Preparation of [Rh(IPr)$_2$(CO)(OAc)] (2). A solution of IPr (56.0 mg, 0.144 mmol) in THF (3 mL) was prepared in the glovebox. To this was added a solution of [Rh(CO)$_2$(OAc)]$_2$ (15.7 mg, 0.036 mmol) in THF (2 mL) dropwise. The resulting orange solution was stirred for 4 h and then removed from the box and filtered through Celite under aerobic conditions. The orange filtrate was concentrated and the resulting solid recrystallized from hexanes and THF. Slow diffusion of hexanes into a THF solution of the yellow powder gave X-ray-quality crystals (yield 42.7 mg, 92%, contaminated with 10−15% of **1**). ^1H NMR (C_6D_6, 400 MHz): δ 7.29 (t, 4H), 7.14 (d, 8H), 6.54 (s, 4H), 3.21 (m, 8H), 1.99 (s, 3H), 1.12 (d, 24H), 0.97 (d, 24H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 191.8 (d, J_{CRh} = 70 Hz, Rh−CO), 190.6 (d, J_{CRh} = 44 Hz, Rh−C_{IPr}), 172. 9, 146.8, 137.9, 129.1, 126.1, 124.0, 34.4, 30.5, 28.2, 26.7, 23.2. IR (KBr): 1952, 1619, 1360. EI MS: m/z 966.49 [M$^+$].

Representative Hydroformylation Experiment: Preparation of (±)-2-Phenylpropanal. In the glovebox, a glass liner was charged with **1** (4.3 mg, 7.1 μmol), PPh_3 (1.8 mg, 7.1 μmol), and styrene (38.0 mg, 0.365 mmol). The mixture was dissolved in 5 mL of benzene, and the solution was stirred briefly. The liner was placed in the autoclave, which contained an additional 2 mL of benzene to prevent unwanted movement of the glass liner. The autoclave was removed from the box, the gauge block assembly attached, and the system pressurized with 500 psi of CO(g) followed by 500 psi of H_2(g). The reaction mixture was allowed to equilibrate to the desired temperature without stirring for 15 min and then stirred at the desired reaction temperature for 19 h, after which the mixture was immediately cooled in an ice bath for 1 h and the pressure released from the autoclave. The contents of the autoclave were transferred to a round-bottomed flask containing a known amount of hexamethylbenzene, as an internal standard, and the liner and autoclave were rinsed with $CDCl_3$. The yield of the reaction was determined by ^1H NMR using solvent suppression techniques to remove the signals for benzene from the spectra.

Determination of Structure by Crystallography. A crystal of the compound of interest (yellow, block-shaped, size 0.40 × 0.30 × 0.20 mm (**1**) and 0.40 × 0.30 × 0.08 mm for (**2**)) was mounted on a glass fiber with grease and cooled to −93 °C under a stream of nitrogen gas controlled with a Cryostream 700 controller. Data collection was performed on a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), operating at 50 kV and 30 mA over 2θ ranges of 4.58−56.64° (**1**) and 2.80−50.00° (**2**). No significant decay was observed during the data collection.

Data were processed on a Pentium PC using the Bruker AXS Crystal Structure Analysis Package, version 5.10.[49] Neutral atom scattering factors were taken from Cromer and Waber.[50] The raw intensity data were integrated using the program SAINT-Plus. Absorption corrections were applied using the program SADABS. The crystal is monoclinic, space group $P2_1/m$, on the basis of the systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-squares refinements minimizing the function $\sum w(F_o^2 - F_c^2)^2$ were applied to both compounds. All non-hydrogen atoms were refined anisotropically. The positions for all hydrogen atoms were located gradually in a difference Fourier map, and their contributions were included in the structure factor calculations.

Convergence to final R1 = 0.0277 and wR2 = 0.0716 for 2573 ($I > 2\sigma(I)$) independent reflections and R1 = 0.0299 and wR2 = 0.0729 for all 2765 (R(int) = 0.0209) independent reflections, with 264 parameters and 8 restraints, was achieved for compound **1**.[51] For compound **2**, convergence to final R1 = 0.0314 and wR2 = 0.0832 for 7356 ($I > 2\sigma(I)$) independent reflections and R1 = 0.0438 and wR2 = 0.0894 for all 9249 (R(int) = 0.0270) independent reflections, with 846 parameters, was achieved. The largest residual peak and hole for **1** were found to be 0.558 and −0.498 e/Å^3, respectively. The largest residual peak and hole for **2** were found to be 0.903 and − 0.344 e/Å^3, respectively.

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Supporting Information Available: Figures, tables, and CIF files giving X-ray crystallographic data for the complexes [Rh(IPr)(CO)$_2$(OAc)] (**1**) and [Rh(IPr)$_2$(CO)(OAc)] (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

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