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Aldehyde Decarbonylation Catalysis under Mild Conditions

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Reaction of $[RhCl(NBD)]_2$ with 2.0 equiv of triphos (triphos = bis(2-diphenylphosphinoethyl)phenylphosphine; NBD = bicyclo[2.2.1]hepta-2,5-diene) in THF solution at room temperature affords [Rh(NBD)(triphos)][Cl] (**4a**), which was isolated as [Rh(NBD)(triphos)]-$[SbF_6]$ (**4b**) in 67% yield. Treatment of **4b** with aqueous formaldehyde in THF solution at 80 °C forms $[Rh(CO)(triphos)][SbF_6]$ (**2a**), which reversibly binds a second equivalent of $CO_{(g)}$ to give $[Rh(CO)_2(triphos)][SbF_6]$ (**2b**). The complex $[Rh(CO)(triphos)][SbF_6]$ has been found to be an effective aldehyde decarbonylation catalyst for primary and aryl aldehydes at temperatures as low as that of refluxing dioxane, with little or no undesirable side products resulting from β elimination or radical rearrangement.

Introduction

Despite much effort, transition metal catalysts for aldehyde decarbonylation[1] still require forcing conditions such as elevated temperature. This is exemplified by the demanding conditions (190−210 °C) required for the decarbonylation of various campholenal derivatives with several transition metal compounds reported by Chapuis.[2]

Although not all catalysts require such high temperatures, even the more effective catalysts for the decarbonylation of aldehydes, Ru(II), Rh(I), and Ir(I) complexes with bis (bidentate phophines),[1a] still require temperatures of 150−180 °C. The synthetic utility of this process would be much enhanced if more active catalysts, effective at lower temperatures, could be found. Transition metal porphyrin complexes[3] have also been shown to be effective decarbonylation catalysts; however, these proceed by a radical mechanism and, as a consequence, are unselective and can give unwanted rearranged products.

As early as 1965, Tsuji[4] reported that the decarbonylation of aldehydes by stoichiometric quantities of Wilkinson's catalyst ($RhCl(PPh_3)_3$) under ambient conditions generates mixtures of alkanes, alkenes, and the stable inorganic product *trans*-$RhCl(CO)(PPh_3)_2$ (**1**). However, attempts to make this system catalytic failed because **1** does not react with aldehydes at temperatures below 200 °C. Complex **1** is believed to be inactive because the electronically depleted Rh(I) center prohibits the necessary oxidative addition of aldehyde C−H bonds and loss of CO is difficult. One approach has been to introduce a reagent that abstracts a CO ligand. In imaginative work, O'Connor[5] has shown that the presence of stoichiometric amounts of the CO abstraction reagent $P(O)(OPh)_2N_3$ allows Wilkinson's catalyst to be catalytic for the decarbonylation of aldehydes at room temperature; however, the process was limited to primary aldehydes. In addition, intriguing results by Goldman[6] suggest that the dimeric species $Rh_2(PMe_3)_2(CO)_2Cl_2$ is an active aldehyde decarbonylation catalyst by direct oxidative addition of the aldehyde C−H bond, without prior dissociation of any ligands from the complex.

Reported here is the development of a new catalyst, $[Rh(CO)(triphos)][SbF_6]$ (**2a**), which is capable of selective aldehyde decarbonylation at temperatures approaching 100 °C.

Results and Discussion

Catalyst Design and Synthesis. In designing a catalyst for aldehyde decarbonylation, we sought to meet three criteria. The first requirement was to achieve a more electron-rich Rh (I) center than complex **1**, to facilitate oxidative addition of the aldehyde C−H bond. The second objective was to construct a system that would disfavor β elimination and thus prevent the formation of unwanted alkene side products previously

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[1] (a) Doughty, D. H.; Pignolet, L. H. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum: New York, 1983; Chapter 11, pp 343−375. (b) Alyea, E. C.; Meek, D. W. *Catalytic Aspects of Metal Phosphine Complexes*; American Chemical Society: Washington, D.C., 1980; Chapter 4, pp 65−83.

[2] Chapuis, C.; Winter, B.; Schulte-Elte, K. H. *Tetrahedron Lett.* **1992**, *33*, 6135.

[3] (a) Domazetis, G.; Tarpey, B.; Dolphin, D.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1980**, 939. (b) Belani, R. M.; James, B. R.; Dolphin, D.; Rettig, S. J. *Can. J. Chem.* **1988**, 2072.

[4] (a) Tsuji. J.; Ohno, K. *Tetrahedron Lett.* **1965**, 3969. Tsuji, J.; Ohno, K. *J. Am. Chem. Soc.* **1968**, *90*, 94. (b) Tsuji, J.; Ohno, K. *J. Am. Chem. Soc.* **1968**, *90*, 99.

[5] (a) O'Connor, J. M.; Ma, J. *J. Org. Chem.* **1992**, *57*, 5075. (b) O'Connor, J. M.; Ma, J. *Inorg. Chem.* **1993**, *32*, 1866.

[6] Abu-Hasanayn, F.; Goldman, M. E.; Goldman, A. S. *J. Am. Chem. Soc.* **1992**, *114*, 2520.

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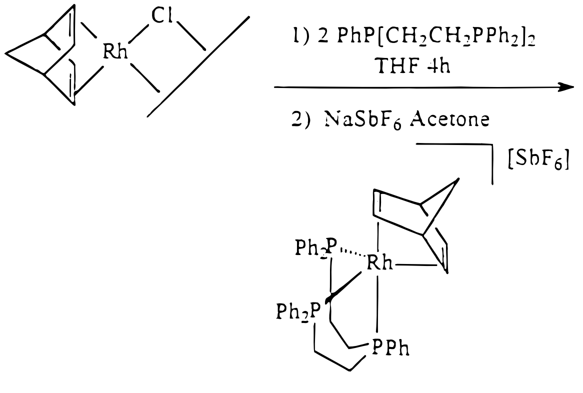
observed with other decarbonylation catalysts. Finally, any potential catalyst must be able to expel CO from its coordination sphere in order to prevent catalyst poisoning.

In light of these criteria, we felt a cationic carbonyl complex of Rh(I) that incorporated a tridentate phosphine might offer the best hope of a synthetically useful catalyst, and to accomplish this we chose the commercially available phosphine triphos. We felt that a complex such as $[Rh(CO)(triphos)]^+$ might offer several advantages over both $Rh(CO)Cl(PPh_3)_2$ and the known[1a] high-temperature decarbonylation catalysts such as those reported by Pignolet. First, the three-point coordination of this phosphine would create a more basic metal center than complex **1**. Second, the chelate-enforced coordinative saturation of the metal center following oxidative addition of the aldehyde C−H bond might well serve to prevent β elimination and subsequent formation of alkene byproducts. Last, similar chelating phosphines[7] have been shown to form cationic carbonyl complexes with Rh(I) that undergo reversible coordination of a second equivalent of CO, which might serve as a mechanism to regenerate the catalyst under appropriate reaction conditions (e.g., vigorous reflux or argon purge).

Although [Rh(CO)(triphos)][Cl] has been previously reported,[8] we sought to prepare complex **2** by metathesis of the chloride ligand of RhCl(triphos) in the presence of CO. To prepare RhCl(triphos), we turned to the previous work by Marder et al.,[9] who reported the reaction of $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) with 2 equiv of triphos in either THF at ambient temperatures or refluxing toluene yielded RhCl(triphos) (**3a**). However, our attempts to prepare this compound by treatment of a THF solution of the norbornadiene analogue $[RhCl(NBD)]_2$ with 1.0 equiv of triphos per Rh produced a yellow precipitate of the unexpected kinetic product [Rh(NBD)(triphos)][Cl] (**4a**). We recognized that this kinetic product might be a useful intermediate in the synthesis of our target catalyst, **2**, because of the presence of the chloride ligand in the outer coordination sphere. Clean metathesis of the chloride anion was achieved by treating **4a** with excess $NaSbF_6$, and subsequent purification by silica gel column chromatography afforded the hexafluoroantimonate salt, **4b**, as an analytically pure solid in 67% isolated yield (eq 1). The tetraphenyl borate analogue of this complex (**4c**) was prepared in a similar manner in 75% isolated yield for crystallographic studies.



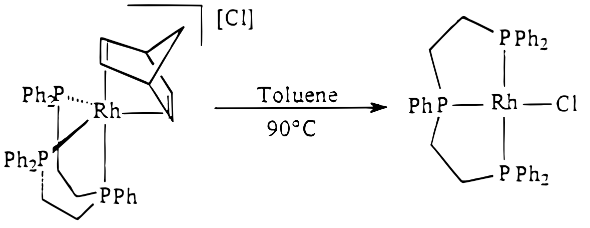
(1)

4b

The ^1H NMR spectrum of **4b** shows the presence of coordinated norbornadiene, which resonates as broad singlets at 3.47, 3.01, and 1.11 ppm, integrating for 4:2:2 protons, respectively. The resonance at 3.47 ppm was assigned to the vinylic protons on the basis of their integration. The ethylene linkages of the triphos ligand appear as the expected overlapping multiplets between 1.90 and 2.95 ppm, integrating to eight protons. The ^{31}P NMR spectrum of **4b** shows a doublet of triplets at 94.9 ppm arising from the central phosphorus atom (P2) coupling to the rhodium center ($^1J_{P-Rh}$ = 121 Hz) and two magnetically equivalent wingtip phosphorus atoms (P1 and P3, $^2J_{P-P}$ = 22 Hz). The wing phosphorus atoms appear as a doublet of doublets resonating at 56.2 ppm ($^1J_{P-Rh}$ = 125 Hz).

Figure 1 shows an ORTEP diagram of the [Rh(NBD)(triphos)] cation, with crystallographic data given in Table 1 and selected bond lengths and angles given in Table 2. The structure is a distorted trigonal bipyramid, with the central phosphorus atom (P2) and the C1−C2 alkene double bond occupying the axial positions and the two wingtip phosphorus atoms (P1, P3) and the C6−C7 alkene double bond occupying the equatorial positions. A similar geometry was reported by Kubiak et al.[10] for [Ir(COD)(triphos)][Cl]. This geometry is probably preferred so as to allow the equatorial alkene ligand to participate fully in back-bonding from Rh(I), which is always strongest in the equatorial position of a trigonal bipyramidal structure. This effect is evidenced clearly in the bond lengths of the equatorial and axial alkenes; that for the equatorial alkene (C6−C7), which participates the most in back-bonding, is 1.418(4) Å, while that for the axial alkene is only 1.378(4) Å long.

On heating in toluene solution at 90 °C for 2 h, [Rh(NBD)(triphos)][Cl] (**4a**) was quantitatively converted into the known compound RhCl(triphos) (**3a**), which was spectroscopically identical to **3a**, as previously reported[9] (eq 2). This result suggests that **4a** is the kinetic product in the reaction of triphos with [RhCl(NBD)]$_2$ to give **3** as the thermodynamic product. Indeed, the norbornadiene ligand of **4b** exchanged with other halides to generate neutral complexes of the type (triphos)RhX, where X = Cl, Br, and I. When **4b** was



(2)

4a **3a**

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(7) Nappier, T. E.; Meek, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 306.

(8) Khan, M. M. T.; Martell, A. E. *Inorg. Chem.* **1974**, *13*, 2961. These authors reported the synthesis by a different route of a compound they suggested was [Rh(CO)(triphos)][Cl]. However, the color, elemental analysis, and ν_{CO} values (ν_{CO} = 1935 cm^{-1}) are all inconsistent with the data reported here. Upon treatment with CO gas, the authors reported the formation of $[Rh(CO)_2(triphos)][Cl]$ with ν_{CO} = 1940, 1975 cm^{-1}, again inconsistent with our data.

(9) Westcott, S. A.; Stringer, G.; Anderson, S.; Taylor, N. J.; Marder, T. B. *Inorg. Chem.* **1994**, *33*, 4589.

(10) Gull, A. M.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1993**, *12*, 2121.

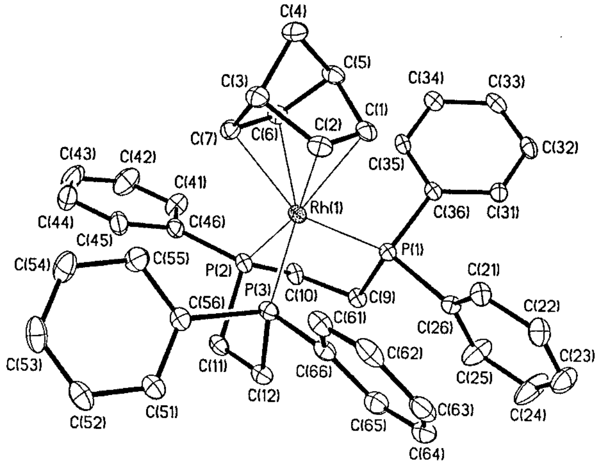


Figure 1. ORTEP diagram of [Rh(NBD)(triphos)][BPh_4] (**4c**), shown with 30% thermal ellipsoids for non-hydrogen atoms.

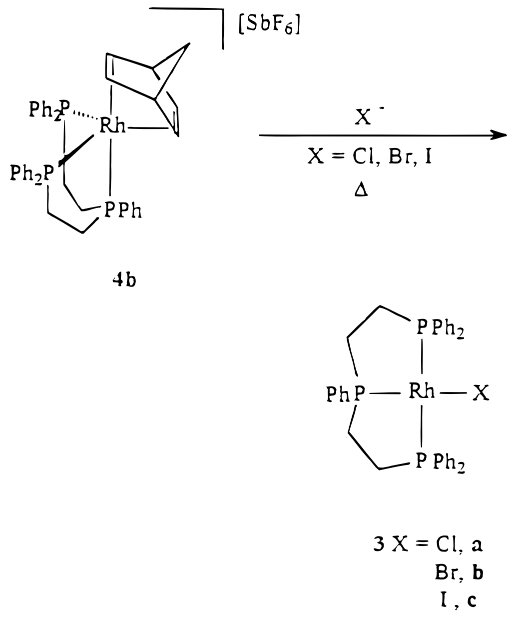
Table 1. Cystallographic Data for [Rh(NBD)(TRIPHOS)][BPh4], 4c

formula	$C_{65}H_{61}BP_3Rh$
fw	1048.77
space group	$P1$
a, Å	14.5339(2)
b, Å	14.6240(2)
c, Å	15.3691(2)
α, deg	106.5730(8)
β, deg	104.7022(2)
γ, deg	113.5455(8)
V, Å^3	2606.77(5)
Z	2
D(calc), g cm^{-3}	1.336
μ(Mo Kα), cm^{-1}	4.61
temp (°C)	−100(2)
radiation	Mo Kα (λ = 0.71−73, Å)
$R(F)$, %^{a}	4.19
$R(wF^2)$, %^{a}	8.91

^{a} Quantity minimized = $R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4c

Rh(1)−C(6)	2.155(3)	Rh(1)−P(1)	2.3558(6)
Rh(1)−C(7)	2.163(2)	Rh(1)−P(2)	2.2428(7)
Rh(1)−C(1)	2.271(3)	Rh(1)−P(3)	2.3461(7)
Rh(1)−C(2)	2.279(3)	C(1)−C(5)	1.531(4)
C(1)−C(2)	1.378(4)	C(3)−C(7)	1.523(4)
C(2)−C(3)	1.528(4)	C(4)−C(5)	1.536(4)
C(5)−C(6)	1.537(4)	C(6)−C(7)	1.418(4)
C(3)−C(4)	1.542(4)		
C(6)−Rh(1)−C(7)	38.35(9)	C(6)−Rh(1)−P(2)	97.03(8)
C(7)−Rh(1)−P(2)	99.41(8)	C(6)−Rh(1)−C(1)	64.29(10)
C(7)−Rh(1)−C(1)	76.03(10)	P(2)−Rh(1)−C(1)	155.59(7)
C(6)−Rh(1)−C(2)	76.06(11)	C(7)−Rh(1)−C(2)	63.49(10)
P(2)−Rh(1)−C(2)	160.08(7)	C(1)−Rh(1)−C(2)	35.26(9)
C(6)−Rh(1)−P(3)	150.10(7)	C(7)−Rh(1)−P(3)	111.84(7)
P(2)−Rh(1)−P(3)	84.19(3)	C(1)−Rh(1)−P(3)	119.95(7)
C(2)−Rh(1)−P(3)	92.68(7)	C(6)−Rh(1)−P(1)	108.84(7)
C(7)−Rh(1)−P(1)	147.13(7)	P(2)−Rh(1)−P(1)	84.04(2)
C(1)−Rh(1)−P(1)	87.41(7)	C(2)−Rh(1)−P(1)	115.84(7)
P(3)−Rh(1)−P(1)	101.02(2)	C(9)−P(1)−Rh(1)	108.15(8)
C(11)−P(2)−Rh(1)	110.25(10)	C(10)−P(2)−Rh(1)	109.63(9)

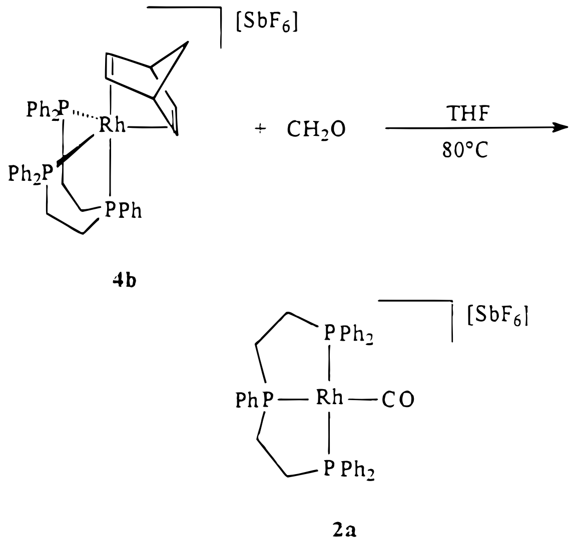


4b

3 X = Cl, **a**
Br, **b**
I, **c**

(3)

heated with alkali halide salts in THF or toluene with stoichiometric quantities of 18-crown-6, complexes **3a**−**c** were obtained in 37−71% isolated yield (eq 3). The substitution of halide for norbornadiene appears to be more facile for the series I > Br > Cl, as is evidenced by the conditions necessary for their synthesis. The reaction of **4b** with chloride required 46 h at 116 °C (toluene, sealed tube), whereas reactions with bromide and iodide required only 48 and 1 h, respectively, at 80 °C in THF (sealed tube). The reactions appeared quantitative by ^{31}P NMR, and the spectroscopic data for these products are shown in Table 3. Despite attempted purification, (triphos)RhCl could not be obtained in analytical purity by this synthesis due to contamination of both water and 18-crown-6; however, both ^1H and ^{31}P NMR spectral data are in agreement with those data previously reported for this compound.[9] Related compounds have been synthesized by Nappier and Meek[7] by reaction of $PhP[CH_2CH_2CH_2PPh_2]_2$ with $[Rh(C_8H_{12})X]_2$ (X = Cl, Br, I) in refluxing ethanol.



4b

2a

(4)

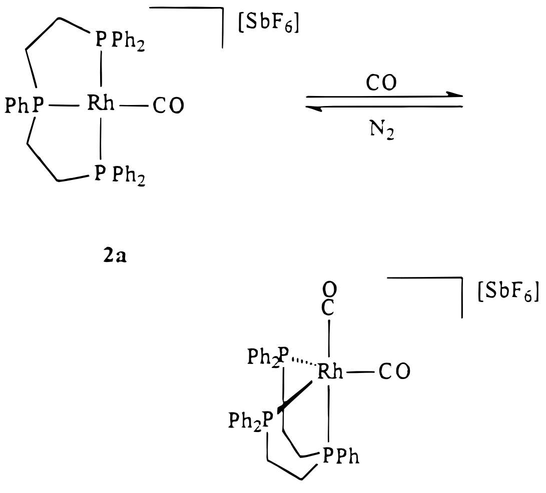
In attempting to prepare our target catalyst **2a**, we were initially disappointed to find that **4b** fails to react directly with CO in THF solution. However, treatment of **4b** with excess aqueous formaldehyde in THF solution at 80 °C for 49 h (sealed tube) resulted in the formation of [Rh(CO)(triphos)][SbF_6], **2a** (eq 4). The ^{31}P NMR spectrum of **2a** shows the expected doublets of doublets for the two magnetically equivalent wingtip phosphorus atoms at 55.0 ppm ($^1J_{P-Rh}$ = 127 Hz, $^2J_{P-P}$ = 28 Hz)

Table 3. ^{31}P NMR Data for the Compounds (triphos)RhX[a]

	trans		cis		
compound	δP2	J(P−Rh)	δP1,P3	J(P−Rh)	J(P−P)
(triphos)RhCl	110.8	164	42.4	143	32
(triphos)RhBr	112.5	167	44.4	142	31
(triphos)RhI	113.0	167	47.8	140	30

[a] Chemical shifts are reported in ppm relative to external 85% H_3PO_4, and coupling constants are reported in hertz.

and a doublet of triplets for the central phosphorus atom at 104.5 ppm ($^1J_{P-Rh} = 116$ Hz). The presence of a carbonyl ligand was established from the strong CO stretching absorption at 2029 cm^{-1} in the IR spectrum of **2a**. When a THF solution of **2a** was treated with carbon monoxide gas at room temperature, a new product was observed by ^{31}P NMR showing a doublet of doublets at 65.4 ppm ($^1J_{P-Rh} = 124$ Hz, $^2J_{P-P} = 22$ Hz) and a doublet of triplets at 105.7 ppm ($^1J_{P-Rh} = 89$ Hz). The IR spectrum of this solution shows two distinct carbonyl stretching absorptions at 2020 and 1968 cm^{-1}, suggesting the presence of a second carbonyl group arising from the coordinatively saturated species [Rh(CO)$_2$(triphos)][SbF$_6$] (**2b**). When a solution of **2b**, prepared as described above, was treated with a stream of nitrogen gas, a ^{31}P NMR spectrum identical to **2a** was obtained, suggesting that the coordination of a second equivalent of carbon monoxide is reversible (eq 5). The IR data reported here are in disagreement with those previously reported for [Rh(CO)(triphos)][Cl],[8] but are in close agreement with those reported for [Rh(CO)(PhP-{CH$_2$CH$_2$CH$_2$PPh$_2$}$_2$)][PF$_6$] by Meek,[7] who also reports reversible CO coordination for this compound.



2a

2b

(5)

Aldehyde Decarbonylations by [Rh(CO)(triphos)][SbF$_6$]. We now find that **2a** is active for the decarbonylation of primary alkyl or aryl aldehydes at temperatures as low as that of refluxing 1,4-dioxane (bp 103 °C). Yields ranging from 15% to 65% were obtained for the stoichiometric (Rh:RCHO, 1:1) decarbonylation of several aldehydes (eq 6). The decarbonylation of

$$\mathbf{2a} + \mathrm{RCHO} \xrightarrow[\text{reflux}]{\text{Dioxane}} \mathrm{RH} + \mathbf{2a} + \mathrm{CO} \qquad (6)$$

primary and aryl aldehydes was found to be more effective than for secondary aldehydes. For example, yields of 57% and 65% were obtained after 40 h for dodecylaldehyde and 4-biphenylcarboxaldehyde to generate undecane and biphenyl, respectively, while the decarbonylation of 2-phenylpropanal generated ethylbenzene in only 15.7% yield under identical conditions. In all cases, only mixtures of unreacted aldehyde and product were observed, and reactions performed in the absence of catalyst under identical conditions showed only starting aldehyde. The absence of products such as undecene and styrene suggests that β elimination does not occur in this system. Examination of the inorganic products by ^{31}P NMR spectroscopy revealed that only compound **2a** is present. This suggests that **2a** is regenerated under the reaction conditions, and this might allow for decarbonylation to become catalytic at modest temperature.

Catalytic decarbonylation of 4-biphenylcarboxaldehyde was achieved in refluxing dioxane, but longer reaction times were needed. Treatment of a 64.2 mM solution of 4-biphenylcarboxaldehyde with 5 mol % **2a** resulted in a 33.7% yield of biphenyl after 94 h (~7 turnovers). Although the rate of decarbonylation in this system is slow, it provides a rare example of a catalyst capable of decarbonylating aldehydes below 110 °C.

Attempts to increase the efficiency of this catalytic reaction by moving to higher temperatures, such as refluxing diglyme (bp 161 °C), were hampered by the partial decomposition of the catalyst. However, despite decomposition, synthetically reasonable yields (43%−100%) were obtained for the decarbonylation of primary and aryl aldehydes in refluxing diglyme after 48 h. Again, as can be seen from the data in Chart 1, yields were lower for secondary aldehydes, with 2-phenylpropanal yielding ethylbenzene in only 18%, with traces (1%) of the β elimination product, styrene.

To investigate the possibility that a radical mechanism could account for the observed decarbonylation, we chose an aldehyde that would serve as a radical trap, citronellal.[6a,11] Under similar catalytic conditions, one product, 2,6-dimethyl-2-heptene, was obtained. The absence of cyclic species such as menthone or isomenthone provides strong support for a nonradical mechanism, such as illustrated in Scheme 1. Such a mechanism would be likely to involve formal oxidative addition of the aldehyde C−H bond at the metal center to generate a metal acyl complex similar to **5**. Complex **5** is then expected to undergo rapid retro-migratory insertion of the acyl R group to generate an alkyl/aryl hydride complex, generically described as compound **6** in Scheme 1. Subsequent reductive elimination would then yield alkane or arene and complex **2b**, in equilibrium with **2a**, completing the catalytic cycle.

Conclusion

Treatment of [RhCl(NBD)]$_2$ with 2.0 equiv of triphos at room temperature results in the kinetic product [Rh(NBD)(triphos)][Cl]. Treatment of [Rh(NBD)(triphos)][SbF$_6$] with aqueous formaldehyde afforded [Rh(CO)(triphos)][SbF$_6$], which exhibits reversible coordination of a second equivalent of CO in solution. The complex

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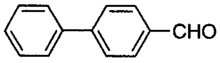
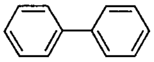
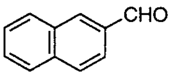
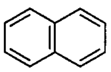
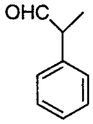
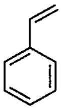
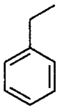
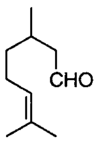
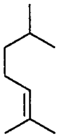
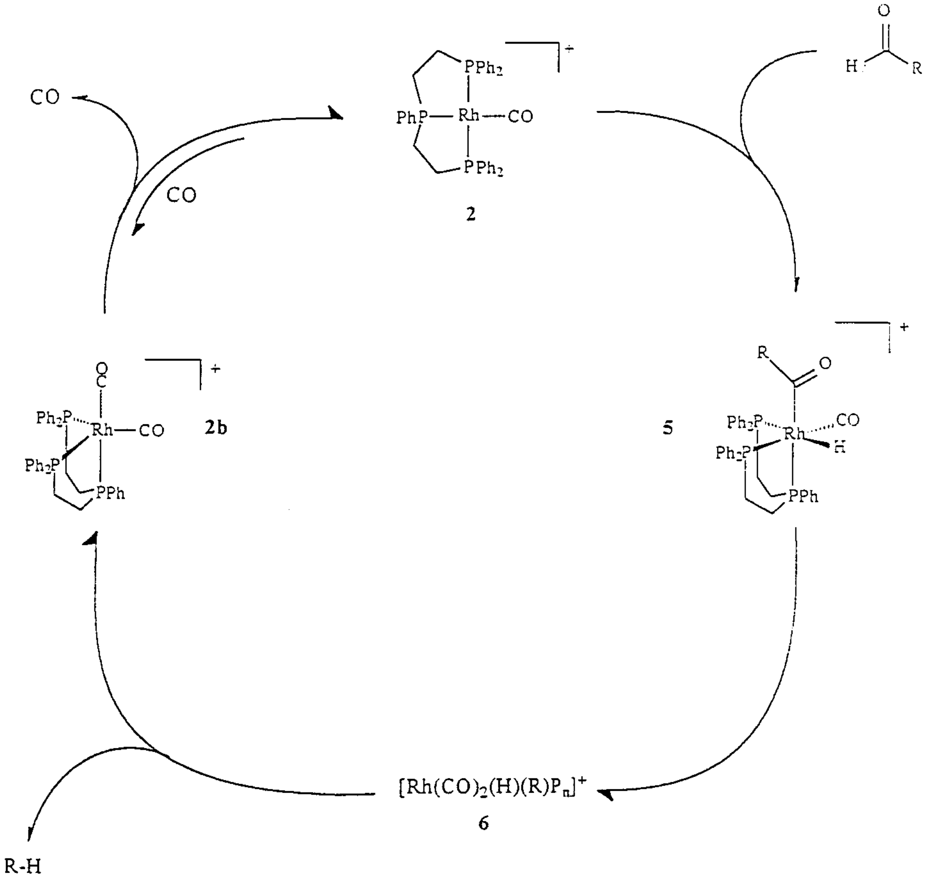
(11) Kampmeier, J. A.; Harris, S. H.; Wedegaertner, D. K. *J. Org. Chem.* **1980**, *45*, 315.

Chart 1

Aldehyde	Product(s)	Conversion (%)	Yield (%)	Time (h)	TOF ($\times 10^{-2}$ turnovers/h)
$CH_3(CH_2)_{10}CHO$	$CH_3(CH_2)_9CH_3$	43 24	100 100	45 24	19 20
		50	100	46	22
		100	100	48	41
	 	19	95, 5	46	8, 0.4
		6	100	46	3

[a] All reactions were performed in refluxing diglyme with 5 mol% **2a**.

Scheme 1



[Rh(CO)(triphos)][SbF6] was found to be an effective catalyst for the decarbonylation of primary and aryl aldehydes under mild conditions with little or no production of unwanted side products resulting from β elimination or radical rearrangement. Preliminary evidence suggests this catalyst functions by formal oxidative addition of the aldehyde C−H bond.

Experimental Section

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 1. A crystal suitable for single X-ray diffraction was obtained by the slow diffusion of pentane into a concentrated sample of **4c** in dichloromethane and mounted on the tip of a capillary with epoxy cement. The data were collected on a Siemens P4 diffractometer equipped with a SMART/CCD detector.

No evidence of symmetry higher than triclinic was observed in the diffraction data. E-statistics suggested the centrosymmetric space group option, $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed by subsequent difference Fourier syntheses, and refined with anisotropic displacement parameters, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.1) program library.[12]

General Procedures. All manipulations were performed in an atmosphere of dry nitrogen or argon using flame-dried glassware and standard techniques unless otherwise noted. Tetrahydrofuran and hexane were freshly distilled from potassium metal prior to use. Dichloromethane was distilled from CaH_2 and stored over activated 4 Å molecular sieves. Deionized water and reagent grade pentane were degassed by three freeze−pump−thaw cycles prior to use. $[RhCl(NBD)]_2$ was synthesized according to literature methods.[13] Triphos was purchased from Aldrich Chemical Co. and used without further purification. NMR spectra were recorded on a GE Omega-300 MHz spectrometer and referenced to residual solvent peaks; ^{31}P NMR (121.6 MHz) spectra were referenced to external 85% H_3PO_4. Chemical shifts are reported in ppm, and coupling constants are reported in hertz. Elemental analyses were performed by Robertson Microlit Laboratories Inc., Madison, NJ.

η^4-(Bicyclo[2.2.1]hepta-2,5-diene)-η^3-(bis(diphenylphosphinoethyl)phenylphosphine)rhodium(I) Hexafluoroantimonate (4b). To a 500 mL round-bottomed flask, equipped with a sidearm, was added $[RhCl(NBD)]_2$ (1.3 g, 2.82 mmol). The solids were then dissolved in THF (30 mL), and triphos (3.02 g, 5.65 mmol), dissolved in THF (45 mL), was added over 10 min via an addition funnel. As the addition was completed, a yellow precipitate formed, and the solution was allowed to stir at room temperature for 4 h, at which point the solution was evaporated to dryness in vacuo. The remainder of the procedure was carried out in air using unpurified, reagent grade solvents. To the solid residue, dissolved in acetone (900 mL) in a 2 L Erlenmeyer flask, was added $NaSbF_6$ (9.60 g, 37.1 mmol) in acetone (200 mL). The solution was then evaporated to dryness in vacuo at room temperature, and the solids were suspended in CH_2Cl_2 (45 mL). The solution was then filtered, and the solids were washed with 3 × 45 mL portions of CH_2Cl_2. The combined CH_2Cl_2 solution was then evaporated to dryness to afford orange solids. The compound was further purified by silica gel column chromatography, first loading the complex in benzene, then washing with benzene (400 mL) to remove organic impurities, and finally eluting with CH_2Cl_2 (ca 1.5 L), until the elutant was colorless. The CH_2Cl_2 fractions were then collected and evaporated to dryness to afford bright yellow solids, which were dried in vacuo overnight. Yield: 3.65 g (67.1%). ^1H NMR (CD_2Cl_2): δ 7.65−6.90 (m, 25H), 3.47 (s, 4H), 3.01 (s, 2H), 2.95−1.90 (m, 8H), 1.11 (s, 2H). ^{31}P NMR (CD_2Cl_2): δ 94.9 (dt, $^1J_{P-Rh} = 121$, $^2J_{P-P} = 22$), 56.15 (dd, $^1J_{P-Rh} = 125$, $^2J_{P-P} = 23$). Anal. Calcd for $C_{41}H_{41}F_6P_3RhSb$: C, 51.03; H, 4.25; F, 11.81. Found: C, 50.88; H, 4.45; F, 11.84.

η^4-(Bicyclo[2.2.1]hepta-2,5-diene)-η^3-(bis(diphenylphosphinoethyl)phenyl-phosphine)rhodium(I) Tetraphenylborate (4c). A procedure similar to that described above was employed, except $NaBPh_4$ was substituted for $NaSbF_6$, and the following quantities were used: $[RhCl(NBD)]_2$ (0.112 g, 0.242 mmol), triphos (0.260 g, 0.486 mmol), THF (8.5 mL), acetone (35 mL), $NaBPh_4$ (0.860 g, 2.51 mmol), CH_2Cl_2 (45 mL) to give a yellow solid. Yield: 0.190 g (75.1%). ^1H NMR (CD_2Cl_2): δ 7.6−6.8 (m, 45H), 3.48 (s, 4H), 2.98 (s, 2H), 2.85−1.8 (m, 8H), 1.08 (s, 2H). ^{31}P NMR (CD_2Cl_2): δ 94.7 (dt, $^1J_{P-Rh} = 121$, $^2J_{P-P} = 23$), 56.3 (dd, $^1J_{P-Rh} = 126$, $^2J_{P-P} = 23$). Anal. Calcd for $C_{65}H_{61}BP_3Rh$: C, 74.37; H, 5.82. Found: C, 74.42; H, 6.01.

Halo-η^3-(bis(diphenylphosphinoethyl)phenylphosphine)rhodium(I) Hexafluoroantimonate (3). Chloro Complex (3a). To a 100 mL bulb equipped with a Kontes valve and magnetic stirrer was added **4b** (300. mg, 0.31 mmol), KCl (150. mg, 2.00 mmol), and 18-crown-6 (150. mg, 0.56 mmol). The solids were then suspended in toluene (30 mL), and the flask was sealed under nitrogen and heated in an oil bath at 116 °C for 46 h. The solids were allowed to settle, and the solution was decanted via cannula into a separate flask while warm. The solution volume was then reduced in vacuo to 10 mL, and solids were obtained by the slow addition of pentane (20 mL), which were then isolated by filtration and vigorously washed with 5 × 5 mL portions of water and 4 × 5 mL portions of pentane. The solids were dried in vacuo at room temperature for 72 h: yellow solids, yield 75 mg (37.3%). ^1H NMR (CD_2Cl_2): δ 8.2−7.3 (m, 25H), 2.7 (m, 4H), 1.75 (m, 4H). ^{31}P NMR (CD_2Cl_2): δ 110.8 (dt, $^1J_{P-Rh} = 164$, $^2J_{P-P} = 32$), 42.4 (dd, $^1J_{P-Rh} = 143$, $^2J_{P-P} = 32$).

Bromo Complex (3b). To a 25 mL bulb equipped with a Kontes valve and magnetic stirrer was added **4b** (300. mg 0.31 mmol), KBr (150. mg, 1.26 mmol), and 18-crown-6 (150. mg, 0.56 mmol). The solids were suspended in THF (15 mL), and the flask was sealed under argon before heating in an oil bath at 80 °C for 72 h. The yellow solution was then decanted via cannula into a separate flask before reducing the solvent volume to ca. 12 mL in vacuo. Yellow solids were obtained by the slow addition of water (25 mL) and isolated by filtration. The solids were then washed with 2 × 3 mL of water and 8 mL of hexane before being dried in vacuo at room temperature for 20 h, and then at 60 °C for 48 h: yellow solids, yield 159 mg (71.4%). ^1H NMR (CD_2Cl_2): δ 8.1−7.3 (m, 25H), 3.0−2.4 (m, 4H), 1.8 (m, 4H). ^{31}P NMR (CD_2Cl_2): δ 112.2 (dt, $^1J_{P-Rh} = 167$, $^2J_{P-P} = 31$), 44.4 (dd, $^1J_{P-Rh} = 142$, $^2J_{P-P} = 32$). Anal. Calcd for $C_{34}H_{33}BrP_3Rh$: C,56.93; H,4.60. Found: C, 56.62; H, 4.83.

Iodo Complex (3c). A similar procedure was employed as described above but with the following quantities: **4b** (300. mg. 0.31 mmol); NaI (140. mg, 0.93 mmol); 18-crown-6 (50 mg, 0.19 mmol); THF (15 mL). Heating was continued for 1 h at 80 °C to afford an orange solution. An orange solid was isolated as described for the bromo complex. Yield: 0.165 g (69.5%). ^1H NMR (CD_2Cl_2): δ 7.9−7.3 (m, 25H), 2.7 (m, 4H), 1.8 (m, 4H). ^{31}P NMR (CD_2Cl_2): δ 113.0 (dt, $^1J_{P-Rh} = 167$, $^2J_{P-P} = 30$), 47.8 (dd, $^1J_{P-Rh} = 139$, $^2J_{P-P} = 29$). Anal. Calcd for $C_{34}H_{33}IP_3Rh$: C, 53.34; H, 4.35; I, 16.60; P, 12.16. Found: C, 53.57; H, 4.66; I, 16.32; P, 12.27.

(Bis(diphenylphosphinoethyl)phenylphosphine)carbonylrhodium(I) Hexafluoroantimonate (2a). To a 100 mL glass bulb equipped with a Kontes valve was added **1b** (0.500 g, 0.524 mmol). The solids were dissolved in 15 mL of THF, and to this yellow solution was added formaldehyde (12.5 mL of a 37% aqueous solution). The flask was then sealed under argon and heated at 80 °C for 49 h. The solution volume was then reduced in vacuo to ca. 15 mL. Yellow solids, obtained by the slow addition of reagent grade pentane (10 mL), were then filtered and washed with pentane (3 × 10 mL) in air and dried in vacuo for 1 h. The compound was then recrystallized from anhydrous THF (ca 3 mL) by the slow addition of reagent grade pentane (10 mL) and then dried in vacuo at 110 °C for 84 h to afford a yellow solid. Yield: 0.170 g (36%). ^1H NMR (CD_2Cl_2): δ 7.8−7.4 (m, 25H), 3.2 (m, 4H), 2.9 (m, 2H), 2.2 (m, 2H). ^{31}P NMR (CD_2Cl_2): δ 104.5 (dt, $^1J_{P-Rh} = 116$, $^2J_{P-P} = 28$), 55.0 (dd,$^1J_{P-Rh} = 127$, $^2J_{P-P} = 28$). IR (NaCl, film, neat): $\nu_{CO} = 2029$ cm^{-1}. Anal. Calcd for $C_{35}H_{33}F_6OP_3RhSb$: C, 46.64; H, 3.66; P, 10.32. Found: C, 46.43; H, 3.84; P, 10.31.

Stoichiometric decarbonylations were performed in a 40 mL flask equipped with a sidearm and charged with **2a** (0.150 g,

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[12] Sheldrick, G. *Siemens XRD*; Madison, WI.

[13] Abel, E. W.; et al. *J. Chem. Soc.* **1959**, 3178.

0.166 mmol), *p*-xylene (as internal standard, 20 μL, 0.163 mmol; in the case of 2-phenylpropanal, 9,10-dihydroanthracene was employed as the standard), 0.17 mmol aldehyde, and 15.0 mL of dioxane to afford a yellow solution. The flask was then fitted with a reflux condenser and an active argon purge established by needle inlet at the top of the condenser and exit gases vented into an oil bubbler. The flask was then lowered into an oil bath and vigorously refluxed for 41.5 h. The flask was then cooled, and an aliquot removed and percolated through silica gel before being analyzed by GC/MS. Product identity was established by comparison of retention time and mass spectra to authentic sample. Reported yields were determined by integration of GC peak area in comparison to internal standard with calibrated detector responses.

Catalytic experiments were performed in a 10 mL flask equipped with a sidearm and charged with **2a** (0.050 g, 0.056 mmol), aldehyde (1.11 mmol), 9,10-dihydroanthracene (as internal standard, 0.100 g, 0.559 mmol), and 5.0 mL of diglyme. A procedure was employed as in the stoichiometric reactions, with the reflux being carried out for 45−47 h. Data for the catalytic decarbonylation of various aldehydes are reported in Chart 1.

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Supporting Information Available: Tables of X-ray crystallographic data for complex **4c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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