each time by vigorous gas evolution. $^{31}P\{^1H\}$ NMR monitoring of the reaction mixture only showed the resonances due to **2b** and **4b**. Therefore, the bimetallic allyl precursor appears to catalyze the formation of distannanes. The structure of **4a** was definitely established by X-ray diffraction (Figure 2).[8] The Fe–Pd–Sn chain makes an angle of 169.34 (2)°, and the Fe–Pd bond is bridged by an unusual μ_2-η^2-alkoxysilyl ligand. The Pd–O bond distance of 216.5 (2) pm, similar to other $Pd^{II}\leftarrow O$ dative bonds,[15] is slightly longer than in in $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})PdCl]$ (210.0 (4) pm), perhaps due to the presence of the bulky $-SnPh_3$ group cis to that bond. The Si–O(4) bond (166.3 (3) pm) is significantly longer than the other two Si–O bonds in this molecule (160.0 (3) and 158.1 (3) pm), consistent with a bimetallic "activation" of this bond. The Pd–Sn distance is in the expected range,[13] and the Fe–Pd distance is shorter than in $[Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(CO)_3(\mu\text{-dppm})PdCl]$, as a combined result of the change in trans ligand and of the bridging mode of the SiOMe group. The latter also causes the geometry at the iron atom to be much more distorted than in **2a**. Thus, while the $Si(OMe)_3$ group is slightly bent away from the Pd atom in **2a**, the Pd–Fe–Si angle decreases to 75.00 (3)° in **4a**. The C(3)–Fe–Si angle (90.3 (1)°) remains about the same as in **2a** (C(2)–Fe–Si = 86.4 (2)°), but the C(3)–Fe–P angle opens by about 8.5°; i.e., the tilt of the $Si(OMe)_3$ group is accompanied by a tilting of the CO ligand trans to the Pd–Fe bond. The ^1H NMR spectroscopic data for **4a** indicate a dynamic behavior for the $-Si(OMe)_3$ group. The high-temperature spectrum (toluene, 363 K) reveals the presence of nine identical protons for the $-Si(OMe)_3$ group, as evidenced by the singlet at δ 3.78. Progressive cooling of the toluene solution broadens this signal until coalescence is reached at ca. 313 K ($\Delta G^{\ddagger} \approx 65 \pm 2$ kJ/mol). A rigid four-membered FePdSiO ring structure with a μ_2-η^2-SiO bridge exists at 243 K, as shown by the prescence of two well-separated singlets for the methoxy protons at δ 3.93 and 3.57 in a 2:1 ratio, respectively, and a further triplet at δ 3.42 for the dppm protons. Although the magnitude of the Sn–P couplings in the ^{31}P and ^{119}Sn NMR spectra is consistent with the molecular structure,[13] it is not clear why $^2J(P\text{-}Sn)$ is smaller than $^3J(P\text{-}Sn)$. With a value of 15.1 ppm, the $^{29}Si\{^1H\}$ NMR chemical shift for **4a**[12] is very similar to that for **2a** (12.9 ppm) and related molecules containing a $-Si(OMe)_3$ group and is consistent with our bonding description, where no silylene-type contribution needs to be invoked.[3]

The reactivity of heterobimetallic allyl complexes[16] such as **2** will be further investigated. Replacement of the allyl group with a ligand occupying only one coordination site on a metal center adjacent to a $M\text{-}Si(OR)_3$ moiety may represent a general access to μ_2-η^2-SiO bonding. The interaction between the hard oxygen donor atom and the soft palladium ion is the most remarkable feature of **4**. Studies are in progress to delineate the electronic and steric factors that favor the formation of such four-membered rings. That this entropically favored intramolecular μ_2-η^2-SiO bridge formation is associated with a hemilabile behavior of the $-Si(OR)_3$ ligand is particularly interesting with respect to the stabilization of unsaturated, reactive polymetallic molecular or surface species.

Acknowledgment. We thank Prof. J. Faller for discussions and the "Commission of the European Communities" (Contract No. ST 2J-0347-C), the CNRS, and the Deutsche Forschungsgemeinschaft for financial support.

Registry No. [K]1, 123674-03-3; **2a**, 132408-39-0; **2b**, 132374-55-1; **3**, 132374-56-2; **4a**, 132374-57-3; **4a**·0.7(toluene), 132486-31-8; **4b**, 132374-58-4; $[Pd(\eta^3\text{-}2\text{-}MeC_3H_4)(\mu\text{-}Cl)]_2$, 12081-18-4; $[Pd(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$, 12012-95-2; $[Pt(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_4$, 123756-28-5; Sn_2Ph_6, 1064-10-4.

Supplementary Material Available: Tables of experimental crystallographic details, final atomic coordinates, thermal parameters, bond lengths, bond angles, and torsional angles for **2a** and **4a** and Figures S-1 and S-2, showing the structures of **2a** and **4a** with the complete labeling scheme (33 pages); listings of observed and calculated structure factor amplitudes for **2a** and **4a** (49 pages). Ordering information is given on any current masthead page.

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[15] For a coordinated water molecule, Pd–O = 220 (1) pm; see: Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490. For a coordinated ketone, Pd–O = 216.3 (3) pm; see: Russel, D. R.; Tucker, P. A. *Ibid.* **1975**, 1743.

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Chemospecific, Biphasic Reduction of α,β-Unsaturated Aldehydes and Ketones Catalyzed by $(Cy_3P)_2Rh(H)Cl_2$

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Summary: The rhodium(III) complex $(Cy_3P)_2Rh(H)Cl_2$ is an effective catalyst precursor for the hydrogenation of the double bond of α,β-unsaturated aldehydes or ketones under mild conditions.

The selective homogeneous catalytic hydrogenation of carbon–carbon double bonds in unsaturated carbonyl compounds, especially aldehydes, has been the object of a number of investigations.[1,2] The highly effective olefin hydrogenation catalyst $[(Ph_3P)_3RuCl_2]$ was shown to be completely inactive in the hydrogenation of unsaturated

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[1] Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis. Practical Application of Transition Metals*; Plenum Press: New York, 1984.

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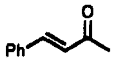
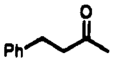
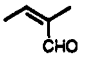
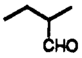
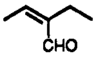
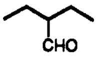
Table I. Hydrogenation of α,β-Unsaturated Carbonyl Compounds by 1 and H_2O or NaOH at 1 atm

substrate (amt, mmol)	amt of 1, mol %	promoter (amt, mL)	organic solvent (amt, mL)	T, °C	time, h	product	GC yield, % (conversn, %)
 (1)	1	0.5 N NaOH (0.5)	benzene (2)	50–55	20		93[a] (100)
 (2)	0.5	0.5 N NaOH (0.2)	benzene (2)	25	11		96 (100)
 (2)	1	0.5 N NaOH (0.2)	benzene (2)	25	18		90 (100)
 (2)	1	H_2O (0.2)	m-xylene (2)	25	22		81 (100)
 (2)[b]	1	H_2O (1)	m-xylene (2)	25	48		95 (100)
 (2)	2	H_2O (0.5)	benzene (2)	35	22		60 (66)
 (2)	1	H_2O (0.2)	m-xylene (2)	25	21		35 (35)
	5	H_2O (0.2)	m-xylene (2)	25	48		90 (100)
 (1)	5	H_2O (0.2)	neat	25	40		15 (15)

[a] Isolated yield. [b] Rhodium metal deposited approximately 24 h after the reaction began.

aldehydes.[3] Wilkinson's catalyst [$(Ph_3P)_3RhCl$] easily decarbonylated aldehydes under mild conditions to give the corresponding hydrocarbon along with catalytically inactive [$(Ph_3P)_2Rh(CO)Cl$].[4] That is why only a few examples of the hydrogenation of α,β-unsaturated aldehydes catalyzed by [$(Ph_3P)_3RhCl$] are known.[3,5,6] These procedures usually require very dilute solutions of substrate, pretreatment of the catalyst with H_2, and induced hydrogen pressure. However, even under such conditions, the catalytic turnover numbers are not very high, and the desired product is often contaminated with byproducts such as hydrocarbons. Some recent publications on the hydrogenation of unsaturated aldehydes with use of ruthenium[7] and iridium[8] complexes reported low chemoselectivity, i.e., simultaneous and independent reduction of both the double-bond and carbonyl functions. Colloidal palladium and nickel can be used sometimes for the selective reduction of aldehydes, but usually heterogeneous reactions are sensitive to many factors such that "...a desired monoreduction of a di- or polyfunctional compound can make the choice of catalyst a rather lengthy decision."[9]

We now wish to report on a highly selective hydrogenation of C=C bonds in α,β-unsaturated ketones and aldehydes catalyzed by the chlorohydridorhodium complex [$(Cy_3P)_2Rh(H)Cl_2$] (Cy = cyclohexyl; 1) under biphasic conditions. Phase-transfer catalysis and biphasic systems have already been used for rhodium-[10] and cobalt-catalyzed[11] hydrogenation of carbon–carbon double bonds in unsaturated ketones, but these catalysts cannot be used in the case of aldehydes. Recently, the system 1–H_2–alkali was shown to effectively catalyze H/D exchange between deuterated arenes and H_2[12] and hydrogenolysis of the carbon–chlorine bond in chloro aromatic compounds.[13] The results of complex 1 catalyzed hydrogenation of α,β-unsaturated ketones and aldehydes are listed in Table I. The hydride 1 itself showed very low activity in the hydrogenation process. Water[14] or 0.5 N NaOH are necessary to promote the generation of the catalytically active species. **For example, conversion of benzylideneacetone (benzene/1% 1; 50–55 °C; 1 atm of H_2; 16 h) was found to be 9% and 91% in the absence and in the presence of 0.5 N NaOH, respectively.** Hydrogenation of crotonaldehyde in dry m-xylene (1% 1; 25 °C; 1 atm of H_2; 4 h) afforded butyraldehyde in only 5% yield, while in the presence of water the yield was 42%. The rate of reactions is significantly dependent on the structure of the substrate. As anticipated, aldehydes with sterically hindered C=C bonds exhibit lower reactivity than crotonaldehyde and cinnamaldehyde. An exception was *trans*-dimethylpropenal, where some rhodium black deposited during the course of this reaction. In no other case was the formation of rhodium metal observed (reaction mixtures remained colored but clear). Saturated carbonyl compounds are the only products of the hydrogenation, and neither alcohols nor hydrocarbons were detected in the reaction mixtures. The catalyst used is able to decarbonylate aldehydes, but at elevated temperature. Reaction of 1 with benzaldehyde or 2-naphthaldehyde in toluene in the presence of H_2 and i-Pr_2NEt as a base (90–95 °C, 15–20 h) led to the corresponding arene and the complex [$(Cy_3P)_2Rh(CO)Cl$] in 60–70% yield. Hence, 1 exhibits quite low activity for the decarbonylation of aldehydes.

The following mechanistic considerations explain the observed results. A reversible coordination of H_2 to 1 followed by reductive elimination of HCl gives the di-

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(14) While very dilute solutions of NaOH are capable of promoting the hydrogenation of unsaturated aldehydes, the resultant saturated aldehydes undergo alkali-induced aldol condensation under these conditions.

hydride [$(Cy_3P)_2Rh(H)_2Cl$] (**2**).[15]

The equilibrium of **1** with **2** (eq 1)[15] can be shifted to the dihydride by the addition of base.[16] Even water is able

$$\underset{1}{L_2Rh(H)Cl_2} + H_2 \rightleftharpoons \underset{2}{L_2Rh(H)_2Cl} + HCl \qquad (1)$$

$$L = Cy_3P$$

to remove HCl from a low-polar organic phase. The monohydride **1** exhibits low catalytic activity, while the dihydride **2** is isostructural and is isoelectronic with [$(Ph_3P)_2Rh(H)_2Cl$], which was shown to be an active catalyst in olefin hydrogenation catalyzed by Wilkinson's complex.[2,17] The absence of any additional phosphine ligands in the present system increases the catalytic activity. On the other hand, bulky tricyclohexylphosphine ligands probably decrease the ability of **2** to decarbonylate aldehydes. In contrast to **2**,[18] monohydride **1** is air-stable and very easy to prepare and use.[13]

In conclusion, complex **1** in the presence of H_2O with or without a base is an efficient catalyst (usually 100/1 ratio of substrate/catalyst) for the highly selective hydrogenation of carbon–carbon double bonds in unsaturated carbonyl compounds, including aldehydes.[19]

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[19] General procedure for the hydrogenation of unsaturated carbonyl compounds: the substrate and an organic/aqueous two-phase system (see Table I for specifics) was placed in a 150-mL Schlenk tube. The monohydride **1** was added, and the mixture was immediately degassed by two freeze-pump-thaw cycles. The Schlenk tube was purged with H_2, and the reaction mixture was stirred under H_2 (see Table I for reaction temperature and time). The organic phase was analysed by GC with an internal standard and by GC-MS. Workup (e.g., 4-phenyl-2-butanone) was effected by separation and concentration. The resulting oil was treated with pentane and then percolated through silica or alumina to give pure product.

Stabilization of Dibenzo-*p*-quinodimethane by (Pentamethylcyclopentadienyl)ruthenium Cation

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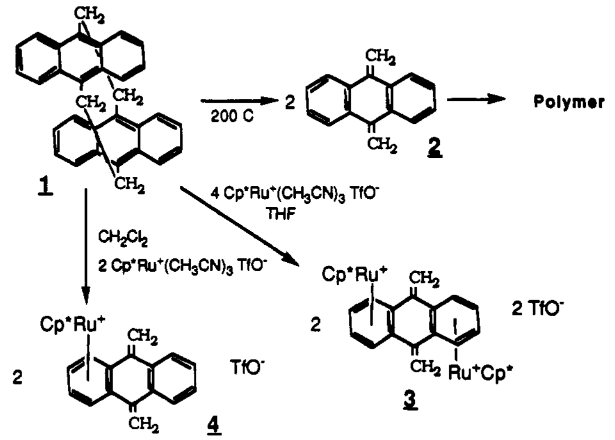
Summary: Reaction of [2.2]anthracenophane (**1**) with [$Cp^*Ru(CH_3CN)_3]^+CF_3SO_3^-$ (Cp^* = η^5-pentamethylcyclopentadienyl) results in cleavage of the ethano bridges to form stable complexes (*trans*-[$(Cp^*Ru)_2(\eta^6{:}\eta^6$-dibenzo-*p*-quinodimethane)]$^{2+}(CF_3SO_3^-)_2$ (**3**) and [$(Cp^*Ru)(\eta^6$-dibenzo-*p*-quinodimethane)]$^+CF_3SO_3^-$ (**4**)) of the highly reactive dibenzo-*p*-quinodimethane (**2**). An X-ray structural analysis of **3** shows the dibenzo-*p*-quinodimethane moiety to be in a boat conformation.

The use of organometallic groups to stabilize otherwise highly reactive organic species has received considerable attention, with the stabilization of cyclobutadiene by iron tricarbonyl ligands being perhaps the paradigm.[1] Molecular orbital calculations show that quinodimethanes have unusually high free valence at the terminal methylene carbons[2] and are consequently highly reactive species that rapidly dimerize or polymerize when generated under normal conditions.[3-5] Several *o*-quinodimethane and similar species stabilized with iron,[6,7] cobalt,[8] and ruthenium[9-12] moieties have been isolated and characterized, but the stabilization of *p*-quinodimethane species presents a particular challenge. Only one type of metal-stabilized *p*-quinodimethane has been reported (two bis(tricarbonyliron) *p*-quinodimethanes), and synthetic yields were very low (<3.5%).[13] [2.2](9,10)-Anthracenophane (**1**) is known to cleave at moderately high temperatures (100–200 °C)[4] to form dibenzo-*p*-quinodimethane (**2**),

Scheme I



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