CO insertion. This dual behavior is in line with the much greater propensity of M–R′ than of M–H to participate in intramolecular CO insertion.[7] It is of further interest that the related binuclear iron nitrosyl anion $[Fe_2(NO)_4(\mu\text{-}PPh_2)_2]^{2-}$[3f] undergoes alkylation (with R′I) at metal with subsequent reductive elimination of $Fe(PPh_2R')$ rather than migratory insertion involving NO.[18] Details of this latter study will be reported separately.

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(Cyclopentadienone)ruthenium Carbonyl Complexes—A New Class of Homogeneous Hydrogenation Catalysts

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Summary: $[(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2$ and $[(\eta^4\text{-}Ph_2Me_2C_4CO)(CO)_2Ru]_2$ represent a new class of efficient precatalysts for homogeneous hydrogenation of alkenes, alkynes, ketones, aldehydes, and anthracene under moderate conditions. Mechanistic aspects have been investigated, and a basic catalytic cycle is proposed.

Many transition-metal complexes function as catalysts in homogeneous hydrogenation reactions.[1] Newly discovered systems may be of interest if they are either exceptionally reactive and inexpensive or if they represent a new class of catalysts carrying interesting mechanistic principles.

Herein we report on a new class of ruthenium homogeneous hydrogenation precatalysts examplified by bis[(η^4-tetraphenylcyclopentadienone)dicarbonylruthenium] (1) and bis[(η^4-2,5-dimethyl-3,4-diphenylcyclopentadienone)dicarbonylruthenium] (2). To the best of

$$\underset{1}{[(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2}$$

$$\underset{2}{[(\eta^4\text{-}Ph_2Me_2C_4CO)(CO)_2Ru]_2}$$

our knowledge, complexes carrying cyclopentadienone (CPD) ligands were not previously recognized as hydrogenation catalysts. The resistance of the CPD ligand to hydrogenation is surprising. Complex 1 was recently reported by us to catalyze an interesting *dehydrogenation* reaction (eq 1).[2] It is a robust, air-stable complex readily prepared in good yield according to eq 2. An X-ray study[3]

$$2RCH_2OH \xrightarrow{1} RCO_2CH_2R + 2H_2\uparrow \qquad (1)$$

$$Ru_3(CO)_{12} + Ph_4C_4CO \rightarrow \underset{3}{(\eta^4\text{-}Ph_4C_4CO)(CO)_3Ru} \xrightarrow{\Delta} 1 + CO \qquad (2)$$

of the previously reported[4] 3 establishes its structural identity. The dimer 1 has, most probably, the structure[5] $\overline{Ru(CO)_2Ph_4C_4CO\rightarrow Ru(CO)_2Ph_4C_4CO}$, similar to that which was proposed for the Fe analogue.[6] The similarly prepared 2 exhibits an IR spectrum [(CCl_4) 2032, 2000, 1977, and 1530 cm^{-1}], which resembles that of 1,[5] and a NMR spectrum [($CDCl_3$) δ 2.06 (s, 6 H), 7.25–7.27 (m, 10 H)] as well as satisfactory elemental analysis.

Table I.[a] **Hydrogenation Data for $[(\eta^4\text{-}Ph_4C_4CO)(CO)_2Ru]_2$**

compd (mmol)	cat. (mmol)	solv (mL)	time, min	% convn[b] (cycles)[c]
1-octene (17.2)	0.01	bulk	10	100 (1720)
2-pentene (46.5)[d]	0.025	bulk	15	100 (1860)
cyclohexene (49.4)	0.025	bulk	15	100 (1976)
cyclohexene (49.4)[e]	0.025	bulk	60	100 (1976)
1-methylcyclohexene (16.9)	0.01	bulk	20	100 (1690)
styrene (52.4)	0.019	bulk	720	67 (2760)
trans-stilbene (10)	0.05	toluene (5)	180	93 (186)
1-hexyne (10)	0.05	toluene (10)	35	100 (200)
4-octyne (10)	0.05	toluene (10)	35	100 (200)
diphenylacetylene (10)	0.05	toluene (10)	135	100 (326)[f]
anthracene (10)	0.05	toluene (10)	135	100[g] (520)
diethyl ketone (95)	0.047	bulk	45	97 (1940)
cyclohexanone (100)[e]	0.05	bulk	300	98 (1960)
diisopropyl ketone (50)	0.025	bulk	180	88 (1760)
dibenzyl ketone (25)	0.025	toluene (5)	180	100 (1000)
acetophenone (50)	0.025	bulk	255	94 (1880)
benzophenone (10)	0.05	toluene (10)	20	49 (96)
benzaldehyde (10)	0.05	toluene (10)	10	81 (162)[h]
pentanal (10)[e]	0.05	toluene (10)	60	100 (200)[i]

[a] Conditions: glass-lined autoclave; 500-psi initial H_2 pressure; temperature 145 ± 1 °C unless otherwise specified. [b] Determined by GC using authentic samples for product identification. [c] Moles of products/moles of catalyst. [d] Cis–trans mixture. [e] Temperature 100 ± 1 °C. [f] The product contained *trans*-stilbene (37%) and 1,2-diphenylethane (63%). [g] A mixture of tetrahydro- and octahydroanthracenes (MS). [h] The products are benzyl alcohol (95%) and benzyl benzoate (5%). [i] The products are 1-pentanol (40%) and *n*-pentyl *n*-pentanoate (60%).

Both 1 and 2 catalyze hydrogenation of various unsaturated substrates (Table I). The following conclusions can be drawn: (a) Complex 1 is a broad spectrum hydrogenation precatalyst for alkenes, alkynes, ketones, aldehydes, and also anthracene. (b) Generally the rates are very good, exceeding, in several cases, 100 cycles/min under moderate reaction conditions, with conversions of 90–100%. (c) Hydrogenation can be carried out in the bulk or in solvent (toluene). (d) Lowering of the temperature diminishes the rate of the reaction. (e) Alkylacetylenes are hydrogenated to the corresponding alkanes. No attempts have yet been made to selectively hydrogenate one bond. (f) Phenyl olefins react slower than alkyl olefins. (g) No hydrogenolysis was encountered. (h) Esters are byproducts in the hydrogenation of aldehydes. Thus, an irreversible bimolecular dehydrogenation (eq 1) of the primary alcohol to ester[7] or alternatively a slow Tish-

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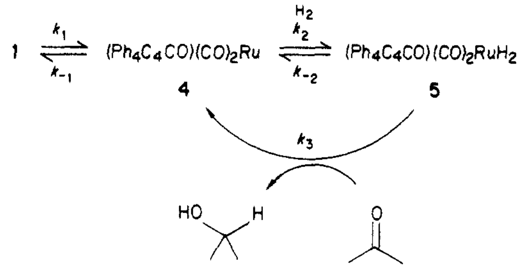
Scheme I



chenko-type disproportionation of the aldehyde[8a] competes with the hydrogenation reaction. (i) Anthracene was quantitatively converted to tetrahydro and octahydroanthracenes identified by MS but not yet fully characterized.

The following additional experiments were performed: (a) Competitive hydrogenation of cyclohexanone and cyclohexene (bulk; 66 °C) gives an initial rates ratio of 8:1, respectively, indicating a moderate chemoselectivity. However, from the table it is evident that cyclohexene is hydrogenated faster than cyclohexanone. This discrepancy can be resolved if one assumes that cyclohexanone binds preferentially (to the complex) but is hydrogenated more slowly than cyclohexene.[8b] (b) (η^4-$Ph_4C_4CO)(CO)_3Ru$ (**3**) exhibits catalytic hydrogenation activity that is 3–4-fold smaller than **1**. (c) Visually the reaction mixtures are pale yellow and homogeneous. Several terminal reaction mixtures were subjected to Maitlis' procedure,[9] indicating the absence of heterogeneous catalytically active material. (d) The initial hydrogenation rate ratio (cyclohexanone; 70 °C) with **1** and **2** is 2.7:1, respectively, providing a starting point for further structural modifications of the CPD ligand.

The identity of the active catalytic species is of basic importance. A related important question is whether the CPD ligand is retained by the metal during catalysis or whether **1** is just another precursor of a catalytically active ruthenium carbonyl complex.

We are proposing a basic catalytic cycle shown in Scheme I. The loaded catalyst is the dimer **1**. In our recent report[2] the dihydride **5** was implicated (IR, NMR) as an intermediate in the dehydrogenation process (eq 1). Now we have carried out the following set of experiments: (1) Hydrogenation of cyclohexanone (1 M) with **1** (5×10^{-3} M) in toluene at 85 °C and H_2 (12 atm) was quantitatively monitored (IR[10] and GC). All along the conversion of ketone → alcohol the room-temperature IR spectrum of the reaction mixture exhibits bands of the dimer **1** *only* (2040, 2010, 1980, 1970 sh, 1550 cm^{-1}). But as soon as all the substrate was consumed (GC; 60 min), the above spectrum cleanly changed into that of the hydride **5** (2025, 1965, 1550 vw cm^{-1}). Clearly, **5** must function as an intermediate and the rate of hydrogen transfer (k_3) must be faster than the oxidative addition of hydrogen to **4** (k_2). (2) A solution of **1** (5×10^{-3} M) in toluene (no substrate) was hydrogenated at 85 °C under H_2 (12 atm). After 90 min a mixture of **1** (43%) and **5** (57%) was obtained (IR). Three experiments, monitored by IR, were performed at room temperature with the above solution. Noteworthy are the exceptionally clean transformations and the homogeneity of the solutions at all times. (a) A slow transformation of **5** → **1** was observed when the above solution was kept under nitrogen. A composition of **1** (57%) and **5** (43%) was obtained after 25 min and 100% of **1** after 4 h. Thus, **5** is also capable of a slow thermal release of H_2 (k_{-2}) that is by far slower than the chemical transfer of H_2 (k_3) (experiment 1). (b) A second portion of the original solution was purged with nitrogen (5 min) to remove soluble hydrogen gas. Subsequent addition of a drop of cyclohexanone has *instantaneously* changed the original mixed composition IR spectrum to that of **1** only; a minute quantity of cyclohexanol was recorded (GC). In the present experiment the oxidative addition of hydrogen (k_2) and the transfer of hydrogen (k_3) were separated and carried out stoichiometrically. Again the latter step proved to be a fast process. (c) Experiment b was repeated with a third portion of the original solution, but nitrogen was now substituted with CO gas. Again a slow thermal transformation of **5** → **1**, accompanied by even slower formation of $(Ph_4C_4CO)(CO)_3Ru$ (~1% at 0.5 h), was recorded. Subsequent addition of a drop of cyclohexanone induces an instantaneous disappearance of **5**, resulting in a composition of **1** (93%) and $(Ph_4C_4CO)(CO)_3Ru$ (7%). The capturing of **4** with CO upon the stoichiometric reduction of cyclohexanone with **5** supports the intermediacy of **4** in the hydrogenation cycle.

From the linear plots of cyclohexanone reduction vs. time with H_2 and D_2, the ratio $k_H/k_D = 1.18 \pm 0.07$ was determined. Therefore, we are led to the conclusion that the dissociation of the dimer **1** (k_1) is the slowest step in our cycle. This conclusion is supported by the observation of an induction period where hydrogenation was slowed down (55 °C). The following relationship can now be established: $k_3 > k_2 > k_1$; $k_{-1} > k_1$; $k_2 > k_{-2}$.

The above results confirm that the CPD ligand is retained by the various catalytic species during hydrogenation. Furthermore the absolute intensities of the IR bands (CO) of **1** during hydrogenation (experiment 1) are constant within experimental error (±5%). Also TLC analyses of the hydrogenation reaction mixture have indicated the absence of tetracyclone and its hydrogenation products. It is noteworthy that free tetracyclone is hydrogenated with **1** at a rate comparable to that of cyclohexanone. Therefore, the present class of complexes differs in its mode of action from known monoene and diene complexes which do exchange their olefinic ligands with substrates during hydrogenation.[11]

The interaction of the coordinatively saturated hydrido complex **5** with the substrate (ketone) is yet unclear. This problem must await the detailed knowledge of the structure of **5**, which may exist (or react) in the tautomeric form (η^5-$Ph_4C_5OH)(CO)_2RuH$. In this form the proton and the hydride can be transferred to the carbonyl of a ketone, thus circumventing the intervention of a 16-electron intermediate prior to the reduction step.

The infrared stretching bands of both the ring and the metal-coordinated carbonyls of **2** are shifted to lower frequencies compared to those of **1**. This indicates a more electron-rich CPD ring in **2** and consequently a more tightly bound dimer which may account for its lower catalytic reactivity compared to that of **1**.

Acknowledgment. We acknowledge the skillful assistance of Mrs. D. Reshef and Mr. A. Elson (undergrad-

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uate student) and thank the Johnson Matthey Research Center for a loan of $RuCl_3$.

Registry No. 1, 94658-85-2; 2, 96482-50-7; 3, 12321-08-3; 4, 96482-51-8; 5, 96482-52-9; 1-octene, 111-66-0; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; styrene, 100-42-5; *trans*-stilbene, 103-30-0; 1-hexyne, 693-02-7; 4-octyne, 1942-45-6; diphenylacetylene, 501-65-5; anthracene, 120-12-7; diethyl ketone, 96-22-0; cyclohexanone, 108-94-1; diisopropyl ketone, 565-80-0; dibenzyl ketone, 102-04-5; acetophenone, 98-86-2; benzophenone, 119-61-9; benzaldehyde, 100-52-7; pentanal, 110-62-3; octane, 111-65-9; pentane, 109-66-0; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; ethylbenzene, 100-41-4; 1,2-diphenylethane, 103-29-7; hexane, 110-54-3; tetrahydroanthracene, 30551-09-8; octahydroanthracene, 1079-71-6; 3-pentanol, 584-02-1; cyclohexanol, 108-93-0; 2,4-dimethyl-3-pentanol, 5381-92-0; 1-phenylethanol, 98-85-1; diphenylmethanol, 119-61-9; benzyl alcohol, 100-51-6; benzyl benzoate, 120-51-4; 1-pentanol, 71-41-0; *n*-pentyl *n*-pentanoate, 540-07-8; tetracyclone, 479-33-4.

Cyclobutaneone Formation via In Situ Generated Vinylketene Complexes of Chromium

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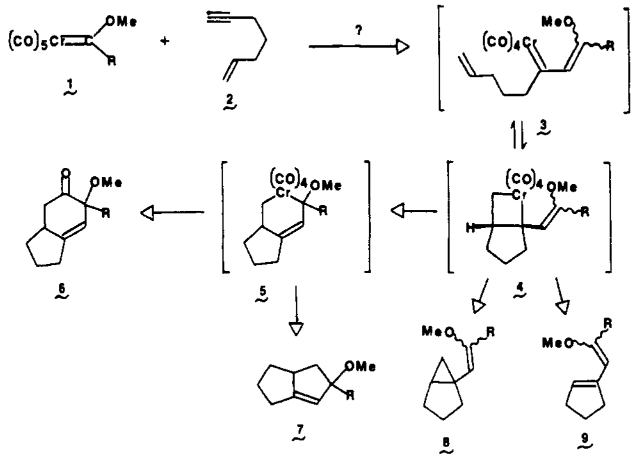
Summary: The reaction of (methoxymethylmethylene)pentacarbonylchromium with 6-hepten-1-yne in acetonitrile proceeds to give two isomeric bicyclo[3.2.0]heptan-6-ones that are substituted in the angular position α to the carbonyl with either an *E* (**10**) or *Z* (**11**) 2-methoxypropenyl group. The reaction with the corresponding tungsten complex fails. The reaction in THF gives a complex mixture of products, the two major of which are the *E* isomer **10** and a trisubstituted furan. There are two reasonable mechanisms to account for the formation of the bicycloheptanones. A methanol-trapping experiment provides evidence for a pathway involving initial reaction of the carbene complex with the acetylene functionality to give a vinylcarbene complex intermediate followed by carbon monoxide insertion to give a vinylketene complex which is then trapped intramolecularly by the olefin to give the bicycloheptanones.

It is well established that chromium Fischer carbene complexes such as 1 will react readily with unactivated acetylenes.[1] Although the heteroatom stabilized chromium carbene complexes such as 1 are unreactive with unactivated olefins,[2] group 6 carbene complexes (probably in high oxidation states) have been strongly implicated in the olefin metathesis reaction which is general for a variety of olefins.[3]

We envisioned a process outlined in Scheme I in which the reaction of an unactivated olefin with a low-valet group 6 carbene complex may be made more favorable. The reaction of complex 1 with an enyne such as 2 would be expected to proceed first with the acetylene functionality to give the intermediate vinylcarbene complex 3[4] in which the intramolecular reaction with an olefin is not only favored entropically but also by the anticipated increased reactivity of this nonstabilized chromium carbene complex.[4,5] According to the accepted mechanism for olefin metathesis,[3] the olefin should add to give the chromacyclobutane derivative 4 which can undergo scission to regenerate either 3 or the new olefin 9. This type of intramolecular metathesis has recently been observed for tungsten complexes.[6] Metallacyclobutane intermediates (W, Cr) have also been demonstrated to undergo reductive elimination to give cyclopropanes from both inter-[2,4,5] and intramolecular[7] reactions of carbene complexes with olefins. The presence of the vinyl group in intermediate 4 may allow for a 1,3-migration of chromium to give the isomeric η^1-allyl species 5. Resonable fates for this intermediate would be reductive elimination to give the bicyclooctene derivative 7 or carbon monoxide insertion and reductive elimination to give the cyclohexenone derivative 6, which would be analogous to the product we have obtained from the reaction of 1a with 1,6-heptadiyne.[8a]

Scheme I



This analysis proved to be only partly correct. The reaction of 1 with enyne 2 does generate intermediates that lead to intramolecular reaction with the unactivated olefin; however, none of the anticipated products indicated in Scheme I could be observed. Instead, the reaction of the methyl complex 1a with enyne 2 in acetonitrile produces the two bicycloheptanones 10 and 11 in 45% yield. The olefin geometry in each case was assigned by NOE difference ^{1}H NMR spectroscopy. Hydrolysis of the mixture of 10 and 11 gave only the angularly substituted dione 12.

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