

energies of activation¹² are, for I, $\Delta G^\ddagger = 3.1 \pm 0.1$ kcal/mol at -138°C ; for II, $\Delta G^\ddagger = 3.0 \pm 0.1$ kcal/mol at -138°C ; for III, $\Delta G^\ddagger = 4.4 \pm 0.2$ kcal/mol at -116°C ; for IV, $\Delta G^\ddagger = 3.1 \pm 0.1$ kcal/mol at -139°C ; for V, $\Delta G^\ddagger = 3.7 \pm 0.1$ kcal/mol at -137°C ; and for VI, $\Delta G^\ddagger = 3.5 \pm 0.1$ kcal/mol at -136°C . Error limits are standard deviations.

The inverse β secondary deuterium isotope effect ($k_1/k_{11} \approx 0.7$ at -138°C) indicates that methyl C-H force constants are greater in the transition state than in the ground state. This implies less hyperconjugation in the transition state than in the ground state.

The rate of the methide shift in VI is between those of the hydride shifts in I and V, reflecting the energy difference between a proton bridge and a protonated cyclopropane, and the conformation change accompanying rearrangement in the six-membered ring. The still lower rate in III may indicate a steric barrier to rotation about the C-3-C-4 bond.

We see no broadening in the ¹³C NMR spectrum of 2-butyl cation at -140°C . Assuming that Δ is 277 ppm, the lower limit for the rate is $4 \times 10^9 \text{ s}^{-1}$ and the upper limit for ΔG^\ddagger is 2.4 kcal/mol.

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- (12) Rate = $(kT/h) \exp(-\Delta G^\ddagger/RT)$.
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Martin Saunders,* Mandes R. Kates

Department of Chemistry, Yale University
New Haven, Connecticut 06520

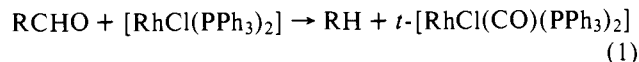
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Catalytic Decarbonylation of Aldehydes

Sir:

Stoichiometric homogeneous decarbonylation of aldehydes using transition metal complexes of *monodentate* tertiary

phosphine ligands such as $\text{RhCl}(\text{PPh}_3)_3$,¹⁻³ $[\text{Rh}(\text{PPh}_3)_2(\text{solvent})_n]^+$,⁴ and $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]^+$ ⁵ is now well established. Of these, $\text{RhCl}(\text{PPh}_3)_3$ (**1**) has received the most study and has proved useful as a reagent in organic synthesis.^{6,7} The basic reaction is thought to occur through the three-coordinate intermediate $[\text{RhCl}(\text{PPh}_3)_2]$:



Small amounts of alkenes and H₂ are also formed from higher saturated aldehydes; for example, 14% 1-hexene is produced from heptanal.² The mechanism for the stoichiometric decarbonylation is presumably similar to that proposed for acyl halides.^{7,8} The reaction cannot be made sufficiently catalytic at useful temperatures because *t*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ does not lose carbon monoxide and the active species $[\text{RhCl}(\text{PPh}_3)_2]$ cannot be regenerated thermally⁹ or photochemically.¹⁰ The decarbonylation reaction can be made catalytic for high boiling aldehydes with **1** or *t*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (vide infra) at temperatures $>200^\circ\text{C}$,⁶ but CO loss is proposed² to occur from the acyl intermediate, which results from oxidative addition of aldehyde to *t*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. Results reported in this communication will show that clean homogeneous *catalytic* decarbonylation of aldehydes using *cationic* rhodium(I) complexes of *chelating* diphosphine ligands occurs at temperatures considerably lower than with **1** and with long-term catalyst stability.

Since a key step in catalytic decarbonylation is the expulsion of coordinated CO and regeneration of the active catalyst, it seemed reasonable to explore the reaction chemistry of aldehydes with *cationic* complexes of *chelating* diphosphine ligands. Such complexes should bind CO much less strongly than *t*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ owing to decreased Rh-CO π back-bonding. This should result because the cationic complexes are less electron rich and likely to have trans rhodium-phosphorous stereochemistry. Accordingly, the complexes $[\text{Rh}(\text{dppe})_2]\text{Cl}$ (**2**) and $[\text{Rh}(\text{dppp})_2]\text{Cl}$ (**3**) where dppe = 1,2-bis(diphenylphosphino)ethane and dppp = 1,2-bis(diphenylphosphino)propane were synthesized¹¹ and reacted with benzaldehyde and heptanal under several conditions of temperature and solvent.¹³ In a typical experiment ~ 20 mg of **2** or **3** was dissolved in 30 mL of a solution consisting of either neat aldehyde or ~ 2 mL of aldehyde in *m*-xylene or toluene. The homogeneous solution was stirred at constant temperature and continuously purged with purified nitrogen gas. The products were collected continuously in a trap connected to the end of a reflux condenser and quantitatively analyzed by GLC. The identity of the organic products was verified by comparison of GLC retention times with those of authentic samples.¹⁴ The results are shown in Table I. All experiments were repeated several times and the data reported in Table I are typical. The results of experiments using **1** or *t*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ are also presented in Table I for comparison purposes and because these data have not been previously reported in the literature. Control experiments were run under identical conditions except without the rhodium catalyst present and *no* decarbonylation products were observed.

It is apparent that the catalytic activities using **2** or **3** are much greater than those using **1**. Indeed, catalytic activities even approaching 100 with **1** or *t*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ are achieved only at temperatures in excess of 230°C .² Additionally, **2** and **3** exhibit long-term stability. Reactions have been run for as long as 1 week with constant catalytic activities and turnover numbers of 100 000 have been achieved, although much higher turnovers are certainly possible. The per cent yield based on aldehyde is 100% for benzene production from benzaldehyde. Hexane is the only volatile product obtained from heptanal. Although it is desirable to achieve catalytic decarbonylation

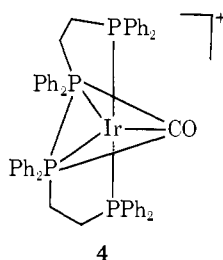
Table I. Catalytic Decarbonylation of Aldehydes Using Complexes **1**, **2**, and **3**

aldehyde (mmol)	catalyst (mmol)	reaction		product (mmol)	catalytic activity, ^a mol of product/mol of catalyst/h
		temp, °C	time, h		
benzaldehyde (neat) ^b	3 (0.00187)	178	46.3	benzene (93.2)	1.1 × 10 ³
benzaldehyde (neat)	2 (0.0122)	178	41.0	benzene (120)	2.4 × 10 ²
benzaldehyde (neat)	1 ^c (0.0119)	178	34.5	benzene (4.05)	9.9
benzaldehyde (neat)	3 (0.0104)	150	21.6	benzene (21.9)	1.0 × 10 ²
benzaldehyde (neat)	2 (0.0360)	150	18.2	benzene (20.2)	30.8
benzaldehyde (neat)	1 ^c (0.0589)	150	29.4	benzene (1.04)	0.60
benzaldehyde (30.0) ^d	3 (0.00405)	140	46.0	benzene (10.6)	5.7 × 10 ¹
benzaldehyde (neat)	2 (0.0321)	140	16.6	benzene (4.50)	8.5
heptanal (37.2) ^d	2 (0.0546)	140	25.2	hexane (5.51)	4.0
benzaldehyde (neat)	1 ^c (0.0437)	140	25.5	benzene (0.136)	0.12
benzaldehyde (30.0) ^e	3 (0.00700)	115	45.7	benzene (3.38)	1.1 × 10 ¹
benzaldehyde (30.0) ^e	2 (0.0189)	115	51.0	benzene (3.50)	3.6
heptanal (52.0) ^e	3 (0.0165)	115	24.0	hexane (12.4)	3.1 × 10 ¹

^a The catalytic activities reported are for specific experiments; however, all values are constant within ±15% for at least 2 days of reaction and for different concentrations and catalyst preparations. ^b The reaction vessel contained 30 mL of solution. ^c The same results were obtained using *t*-RhCl(CO)(PPh₃)₂ as the catalyst. ^d Experiments were carried out in refluxing *m*-xylene. ^e Refluxing toluene.

with higher activities at lower temperatures, the results obtained with **2** and **3** represent a marked improvement over any compounds studied to date and suggest that a systematic variation in the nature of the chelating diphosphine ligand should lead to greater catalytic activities (vide infra).

It is interesting that reaction of **2** with CO does not give an isolable metal carbonyl compound.¹⁵ [Rh(dppe)₂]⁺ is consistently isolated presumably as an aldehyde solvate from the catalytic reaction mixtures using **2** (Table I) and there is no spectroscopic (IR) evidence for Rh-CO bonding. However, CO is known to react with **3** forming [Rh(CO)(dppp)₂]⁺,¹⁵ and small amounts of this species are detected when the reaction is quenched. It is premature to speculate on the reaction mechanism without further experimentation; however, it is likely that CO loss from an intermediate is quite facile and that oxidative addition of aldehyde RC(O)H or R group migration is the rate-limiting step. The analogous iridium complex [Ir(dppe)₂]⁺ is known to bind CO reversibly in solution.¹⁶ The structure of the CO adduct [Ir(CO)(dppe)₂]⁺ **4** has been de-



termined by X-ray analysis¹⁷ and is distorted trigonal-bipyramidal with CO occupying an equatorial position. It has been suggested that [Rh(CO)(dppp)₂]⁺ has the same structure.¹⁵ Additionally, there have been several reports on oxidative addition of H₂, O₂, and HCl to various square-planar rhodium(I) and iridium(I) bis(diphosphine) cationic complexes.^{12,15,16,18} Since the slow step in the catalytic decarbonylation reaction using **2** or **3** is likely to be oxidative addition or R group migration, experiments using more basic and more flexible chelating ligands such as 1-phenylenebis(dimethylarsine) or 1,2-bis(diphenylphosphino)butane may give higher catalytic activities. Indeed, decarbonylation rates increased significantly on going from dppe to dppp (Table I) indicating that ligand flexibility is an important factor. Experiments using these and other chelating diphosphine and diarsine ligands are in progress.

Homogeneous catalytic hydrogenation reactions using **1** are known to be photoassisted,¹⁹ and therefore it seemed reasonable to determine if catalytic decarbonylation rates using **1** and

2 are accelerated by continuous UV irradiation. The catalytic activity for benzene production from neat benzaldehyde using **1** (10⁻³ M) at 150 °C with continuous irradiation through Pyrex glass was increased by a factor of 3.0 over the thermal rate. A 100-W medium-pressure mercury vapor lamp (type SH, with a reflector and placed ~5 in from reaction vessel) was used and the reaction was run for 20 h with the photoassisted catalytic activity. The catalytic activity of the irradiated solution returned to its usual thermal value after completion of photolysis. No benzene was produced during irradiation experiments run under identical reaction conditions except without the catalyst present. Surprisingly, the catalytic decarbonylation of benzaldehyde using **2** under the above reaction conditions was *not* photoassisted. It is likely that the photoassistance observed with **1** occurs because of photoinduced CO or PPh₃ expulsion from the acyl intermediate RhCl(CO)-H[C(O)Ph](PPh₃)₂, whereas CO loss from an intermediate such as "[Rh(CO)(dppe)₂]⁺" would not be rate limiting (vide supra). It is interesting that the catalytic decarbonylation of benzoyl chloride (to chlorobenzene) using **1** is *not* photoassisted.²⁰ We have confirmed this result for the above experimental conditions. It is clear that subtle electronic and steric changes can impart marked reactivity differences. Work in progress is aimed at determining the mechanism for the catalytic decarbonylation reaction using **2** and **3** and at finding new and more effective catalysts.

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- (13) Aldehyde substrates were carefully purified by repeated fractional distillations and were run through an activated alumina column.
 (14) GLC conditions: 8-ft columns packed with 10% Carbowax 20M on Chromosorb GNAW or 10% OV-101 on Chromosorb G.
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D. H. Doughty, L. H. Pignolet*

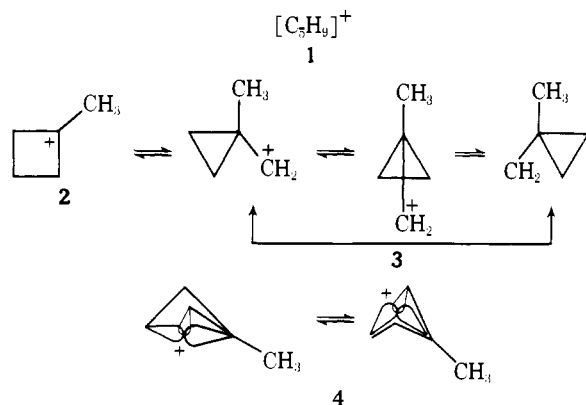
Department of Chemistry, University of Minnesota
 Minneapolis, Minnesota 55455

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Concerning the Structure and Modes of Degenerate Rearrangement of the Nonclassical 1-Methylcyclobutyl and Related Carbocations

Sir:

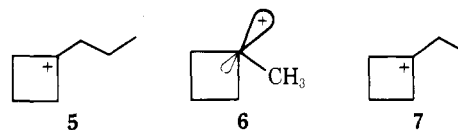
The structure of the 1-methylcyclobutyl cation (**1**) is of dispute.² Based on ¹H and ¹³C NMR spectroscopic studies by Saunders and Rosenfield,³ as well as by Olah et al.,⁴ in which the methylene groups were found to be completely averaged at the lowest temperature studied (ca. -80 °C), it was concluded that ion **1** is best represented as a set of rapidly equilibrating bisected σ -delocalized 1-methylcyclopropylcarbinyl cations (**3**) equilibrating through the classical 1-methylcyclobutyl cation (**2**). In earlier work, Olah et al.^{4a} have also



considered the equilibrating σ -delocalized bicyclobutonium ion (**4**) like structure.

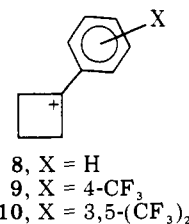
Sorensen and Kirchen² have recently reinvestigated ion **1** by NMR spectroscopy at considerably lower temperatures (ca.

-158 °C). In both the ¹H and ¹³C NMR spectra, the methylene peaks broadened and decoalesced into two separate peaks without affecting the chemical shifts associated with the other two carbon atoms. Similar behavior was also reported for the 1-propylcyclobutyl cation (**5**). From the new, very low temperature observations, Sorensen and Kirchen rightly ruled out the previously suggested^{3,4} equilibrating cyclopropylcarbinyl-1-methylcyclobutyl structures (**2** \rightleftharpoons **3**). They claimed



to have frozen out the static classical 1-methylcyclobutyl cation and suggested that, at higher temperatures, methylene scrambling occurs via equilibration through unpopulated cyclopropylcarbinyl cations (**3**). Since the carbocationic center in **1** as already reported⁴ by us is highly shielded (by 170 ppm) compared with that in typical sp²-hybridized static carbocations such as the 1-methylcyclopentyl cation and other tertiary cycloalkyl cations, Sorensen and Kirchen suggested an sp³-hybridized 1-methylcyclobutyl cation structure (**6**) for an unstrained tertiary cycloalkyl cation.

The suggestion of such an unusual sp³-hybridized classical carbocation structure **6** called for reinvestigation. We have repeated Sorensen and Kirchen's low temperature ¹³C NMR work on ion **1** and also carried out low temperature studies at a higher field (63 MHz for carbon). The results for ion **1** were comparable with those of Sorensen and Kirchen. The 1-ethyl- and 1-propylcyclobutyl cations (**7** and **5**) also behave similarly to ion **1** at -150 °C, but rearrange to substituted cycloalkyl cations at temperatures as low as -130 °C. Whereas the 1-phenylcyclobutyl cation (**8**) as reported previously by us is a



static classical carbocation, the 4-trifluoromethylphenylcyclobutyl cation (**9**) and 3,5-bis(trifluoromethyl)phenylcyclobutyl cation (**10**) were found, upon raising the temperature, to equilibrate through the related, but practically unpopulated (in the Boltzmann distribution) cyclopropylcarbinyl cations which average the methylene carbons similar to ion **1**. The ¹³C NMR shifts of the carbocation centers of ions **10** and **9** at -60 and -34 °C are $\delta(^{13}\text{C})$ 286.4 and 284.1, respectively. The averaged methylene peaks are observed at $\delta(^{13}\text{C})$ 37.8 for **9**

Table I. ¹³C NMR Chemical Shifts^a of Substituted Cyclobutyl Cations

ion	temp, °C	C ⁺	C _α	C _β	methyl	additional groups
1	-74	163.09	48.69	48.69	25.37	
	-156.4	162.08	72.72	-2.83	25.83	
8	-70	271.67	44.95	17.47		Ci, 138.48; Co, 142.28; Cm, 133.17; Cp, 157.40
5	-121	164.41	45.99	45.99	12.68	α^1 -CH ₂ , 39.27; β^1 -CH ₂ , 19.01
7	-130	166.43	merged in the base line		13.00	α^1 -CH ₂ , 36.46
10	-60	286.42	39.64	39.64		Ci, 146.42; Cp, 140.50; Co, 137.70; and Cm, 137.29 ($J_{\text{C}-\text{C}-\text{F}} = 35.7$ Hz); -CF ₃ , 122.90 ($J_{\text{C}-\text{F}} = 273.4$ Hz)
	-123.4	290.11	50.47	17.88		identical with those at -60 °C
9	-114	285.29	47.36	16.86		Ci, 139.69; and Cp, 152.13 ($J_{\text{C}-\text{C}-\text{F}} = 34.7$ Hz); Co, 142.62; Cm, 129.67; and -CF ₃ , 122.80 ($J_{\text{C}-\text{F}} = 278.0$ Hz)
	-34	284.13	37.76	37.76		identical with those at -60 °C

^a Shifts from external capillary Me₄Si in SbF₅/SO₂ClF solutions.