place active species (e.g., cation radicals) or products from the surface also can result in low conversions.

At least two factors complicate the kinetics of NBD production in illuminated $Q/CdS/MV^{2+}/CH_3CN$ suspensions (Table III). The first is competitive and unproductive absorption by a ground state $Q\text{–}MV^{2+}$ complex (Figure 2) whose concentration tracks that of Q (eq 5). Consequently, as the initial Q concentration is increased, a correspondingly larger fraction of the incident radiation is absorbed by the complex. The second factor also involves competitive absorption but, in this case, by one of more photochemically derived species (Figure 2) whose concentration increases as a function of irradiation time. Although these species have not been identified,[27] they appear to play no role in the formation of NBD. Their main effect is to decrease the fraction of light absorbed by the semiconductor particles as photolysis proceeds and thereby cause a steady decline in the rate of NBD production (Table V).

Concluding Remarks

Our main findings can be summarized as follows. (1) Quadricyclene rearranges to its more stable isomer, norbornadiene, in the presence of irradiated n-type semiconductor powders. (2) The key step in the mechanism of this process involves the oxidation of Q to its structurally labile cation radical by photogenerated holes that migrate to the semiconductor surface (Figure 3A). (3) The percentage yield of NBD depends upon the semiconductor in an order, $CdS > TiO_2 \geq ZnO$, which is inverse to that of the band gaps. (4) Addition of the methylviologen dication increases the product yield by capturing photoexcited electrons in the conduction band and thus prolonging the lifetime of the corresponding holes in the valence band (Figure 3B). (5) Addition of the hole relay, diphenylamine, causes a modest increase in the product yield (Figure 3C) but does not appear to facilitate the operation of a catalytic redox chain cycle (eq 2 and 3) in the bulk solution. (6) Solvent effects upon the NBD yield can be attributed to surface phenomena. (7) Although attempts to manipulate the kinetics of electron transfer led to some improvements in system performance (points 4 and 5), the quantum efficiency of NBD production is disappointingly low.

Finally, it should be noted that the present study provides one of the few reported examples of an organic valence isomerization process mediated by an illuminated semiconductor.[28,29]

Acknowledgment. We are grateful to Professor Michael L. Norton for taking the scanning electron micrographs. Financial support for this work was provided by the National Science Foundation (Grant CHE-8210558) and the Oji Paper Company.

Registry No. TiO_2, 13463-67-7; ZnO, 1314-13-2; CdS, 1306-23-6; Ph_2NH, 122-39-4; quadricyclene, 278-06-8; norbornadiene, 121-46-0; methylviologen dication, 64890-16-0.

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[27] The spectral results are not consistent with a significant steady-state concentration of methylviologen cation radical, $MV^{\bullet+}$. See: Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.

[28] For another, very recent, example, see: Al-Ekabi, H.; de Mayo, P. *J. Phys. Chem.* **1986**, *90*, 4075.

[29] (a) The editor kindly called to our attention a very recent paper by Draper and de Mayo[29b] concerning the Q to NBD isomerization in the presence of irradiated CdS and ZnO. The observations of these workers agree in essential detail with those reported here and lend additional support to the intermediacy of photogenerated cation radicals in the mechanism of isomerization. (b) Draper, A. M.; de Mayo, P. *Tetrahedron Lett.* **1986**, *27*, 6157.

Partial Loss of Deuterium Label in Wilkinson's Catalyst Promoted Decarbonylations of Deuterioaldehydes

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Decarbonylations of *trans*-2-phenylcyclopropanedeuteriocarboxaldehyde and cycloheptanedeuteriocarboxaldehyde with Wilkinson's catalyst give phenylcyclopropane and cycloheptane with partial loss of deuterium label. Loss of deuterium label is not a consequence of orthometalation of deuteriotris(triphenylphosphine)rhodium(I), a plausible reactive intermediate, for the loss is observed even when $RhCl(P(C_6D_5)_3)_3$ is used to effect the decarbonylation. Decarbonylations of *trans*-2-phenylcyclopropanecarboxaldehyde with Wilkinson's catalyst in benzene containing *O*-deuterioethanol afford d_0 and d_1 phenylcyclopropane and d_0 and d_1 aldehyde; neither hydrocarbon product nor recovered aldehyde is deuterium labeled when 1,1-dideuterioethanol is present in the decarbonylation reaction mixture. The hydroxyl hydrogen of ethanol associated with $RhCl(P(C_6H_5)_3)_3$ as normally synthesized, however, is not the hydrogen source: ethanol is not detected by ^1H NMR in solutions of the catalyst, loss of deuterium label occurs even when $RhCl(PPh_3)_3$ is prepared free of possible contamination by ethanol from $[ClRh(C_2H_4)_2]_2$, and it is seen as well with an alternative ethanol-free decarbonylation catalyst, $ClRh(dppp)_2$. The hydrogen source is water retained in commercial Wilkinson's catalyst. Decarbonylations of deuterioaldehyde in the presence of excess D_2O give d_1 product with high preservation of label.

The facile decarbonylation of aldehydes[2,3] effected by Wilkinson's catalyst, tris(triphenylphosphine)rhodium(I) chloride,[4] now enjoys an established position in organic synthesis, for it is widely applicable and highly stereose-

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[1] Syracuse University.

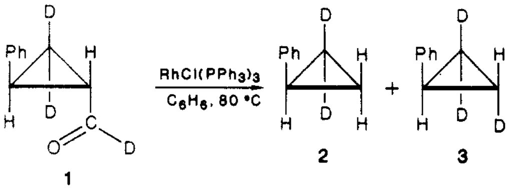
[2] Tsuji, J.; Ohno, K. *Tetrahedron Lett.* **1965**, 3969–3971. Tsuji, J.; Ohno, K. *Tetrahedron Lett.* **1967**, 2173–2176. Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99–107.

[3] Baird, M. C.; Lawson, D. N.; Mague, J. T.; Osborn, J. A.; Wilkinson, G. *Chem. Commun.* **1966**, 129–130. Baird, M. C.; Nyman, C. J.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 348–351.

[4] Jardine, F. H. *Prog. Inorg. Chem.* **1981**, *28*, 63–202.

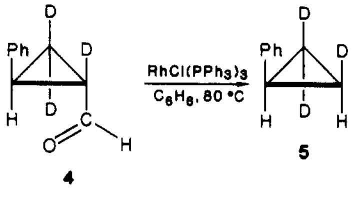
lective.[5-7] Decarbonylations of deuterioaldehydes have been reported to give 100% of the deuterium label in the hydrocarbon product,[7-9] thus demonstrating an attractive potential for preparing deuteriated hydrocarbons in a convenient and stereoselective manner.

In the course of synthetic work leading to various deuterated phenylcyclopropanes[10] we encountered a substantial loss of deuterium label during the Wilkinson's catalyst promoted decarbonylation of a deuterioaldehyde. The trideuterio-substituted aldehyde 1, prepared from the corresponding 3,3-dideuterio carboxylic acid through reduction with lithium aluminum deuteride followed by oxidation with pyridinium chlorochromate, was treated with 1 equiv of $RhCl(PPh_3)_3$ in benzene at reflux: the reaction product proved to be a mixture of phenylcyclopropanes 2 and 3. Chemical shift values for C(2,3) protons cis and trans to the phenyl group in phenylcyclopropane are 0.65 and 0.89 ppm, respectively.[11] The mol % of 2 in product mixtures from three runs was estimated by ^1H NMR spectroscopy to be 45 ± 4 despite quantitative incorporation of deuterium at the carbonyl carbon of 1.



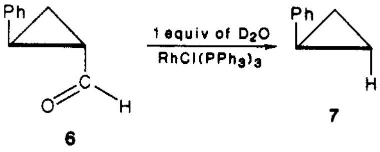
Two lines of evidence supported the assignment of the unanticipated absorption intensity at 0.89 ppm in the product mixture derived from 1 to structure 2: repeated purification of the product by preparative VPC on Carbowax, Apiezon L, and SE-30 columns did not alter the intensity ratios, and analogous decarbonylations with protioaldehydes (e.g., 4 → 5) gave products with excellent stereoselectivity and without spurious NMR signals in the upfield region from byproducts.[10]

This alternative synthetic approach, decarbonylation of α-deuterio aldehydes rather than deuterioaldehydes, proved fully adequate to our immediate preparative needs:[10] but the question posed by 1 → 2 remained to be pondered, and answered.

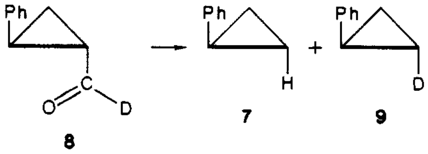


Results

A cursory test to see whether water was the proton source was conducted with unlabeled aldehyde 6 in the presence of 1 equiv of D_2O; ^1H NMR spectroscopic scrutiny of the phenylcyclopropane product provided no clear evidence of deuterium incorporation.



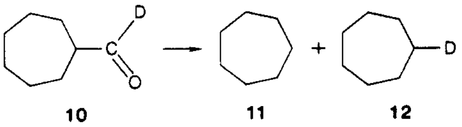
Substantial loss of deuterium label during decarbonylations of deuterioaldehydes was confirmed with *trans*-2-phenylcyclopropanedeuteriocarboxaldehyde (8). Analyses of decarbonylation reaction mixtures by gas chromatography/mass spectrometry rather than by chromatography followed by NMR spectroscopy showed again that both d_0 and d_1 phenylcyclopropane were obtained.



In a series of small scale runs using 1 equiv of catalyst from Strem Chemical in benzene at 50–80 °C, no temperature dependence in product d_0/d_1 ratio was seen, but more dilute solutions gave more d_1 phenylcyclopropane. For five runs at aldehyde 8 concentrations of 0.10–0.12 M, 86 ± 1% of phenylcyclopropane product had lost deuterium label; for four runs at [8] = 0.02 M, the product showed 45 ± 5% loss of label; for a single run at [8] = 0.01 M, the loss was 35%.

Two other commercial samples of Wilkinson's catalyst were used, and the deuterium loss persisted; 0.2 M 8 with Aldrich standard grade or with Gold Label catalyst gave 66 ± 1% loss of label while a parallel reaction using the Strem catalyst exhibited 73% of d_0 product 7 in the phenylcyclopropane mixture.

Loss of deuterium label was also observed in the decarbonylation of cycloheptanedeuteriocarboxaldehyde (10). Decarbonylation with Strem Chemical Wilkinson's catalyst gave cycloheptane product with 13 ± 4% loss of label (seven runs, [10] = 0.2–0.01 M). The extent of the loss was far less significant than observed for decarbonylations of 8, yet it did definitely occur. The loss of label from deuterioaldehydes during decarbonylations with $RhCl(PPh_3)_3$ is thus not limited to substrates 1 and 8, but the magnitude of the loss appeared to be substrate dependent.



Attempts to secure reproducible data to define the apparent concentration vs. % loss of label dependence were frustrated by intermittent incursions of outliers. For instance in one set of 19 decarbonylations of 8, 15 of the runs

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(5) Tsuji, J.; Ohno, K. *Synthesis* **1969**, 157–169. Tsuji, J. *Org. Synth. Met. Carbonyls* **1977**, *2*, 595–654.

(6) Inter alia: Dawson, D. J.; Ireland, R. E. *Tetrahedron Lett.* **1968**, 1899–1901. Ireland, R. E.; Pfister, G. *Tetrahedron Lett.* **1969**, 2145–2148. Hill, R. K.; Cullision, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 1229–1239. Trost, B. M.; Bogdanowicz, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 2038–2040. Trost, B. M.; Preckel, M. *J. Am. Chem. Soc.* **1973**, *95*, 7862–7864. Hobbs, P. D.; Magnus, P. D. *J. Chem. Soc., Chem. Commun.* **1974**, 856–857. Letourneux, Y.; Büjüktür, G.; Ryzlak, M. T.; Banerjee, A. K.; Gut, M. *J. Org. Chem.* **1976**, *41*, 2288–2292. Anastasia, M.; Fiecchi, A.; Cighetti, G.; Galli, G. *J. Chem. Soc., Perkin Trans. 1* **1977**, 700–702.

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(8) Kampmeier, J. A.; Harris, S. H.; Wedegaertner, D. K. *J. Org. Chem.* **1980**, *45*, 315–518.

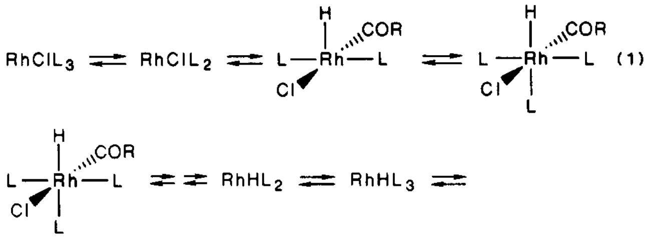
(9) Deuterioaldehydes are easily made: Kühlein, K.; Neumann, W. P.; Mohring, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 455–457. Kuivila, H. G. *Synthesis* **1970**, 499–509. Walborsky, H. M.; Morrison, W. H.; Niznik, G. E. *J. Am. Chem. Soc.* **1970**, *92*, 6675–6676. Fleet, G. W. J.; Fuller, C. J.; Harding, P. J. C. *Tetrahedron Lett.* **1978**, 1437–1440. Fleet, G. W. J.; Harding, P. J. C. *Tetrahedron Lett.* **1979**, 975–978. Sorrell, T. N.; Spillane, R. J. *Tetrahedron Lett.* **1978**, 2473–2474. Sorrell, T. N.; Pearlman, P. S. *J. Org. Chem.* **1980**, *45*, 3449–3451. Guibe, F.; Four, P.; Riviere, H. *J. Chem. Soc., Chem. Commun.* **1980**, 432–433. Four, P.; Guibe, F. *J. Org. Chem.* **1981**, *46*, 4439–4445.

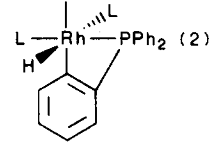
(10) Baldwin, J. E.; Patapoff, T. W.; Barden, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1421–1426. Baldwin, J. E.; Barden, T. C. *J. Amer. Chem. Soc.* **1984**, *106*, 5312–5319; **1984**, *106*, 6364–6367.

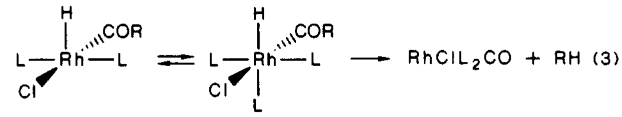
(11) Wiberg, K. B.; Barth, D. E.; Schertler, P. H. *J. Org. Chem.* **1973**, *38*, 378–381.

gave 76 ± 2% loss of label over a [8] range 0.2–0.02 M. The other four values were 14%, 34%, 35%, and 36%.

We supposed, at this point, that loss of deuterium during the overall conversion **8** → **7** might be caused by an orthometalation side reaction,[12] a process for which there is ample precedent in hydridotris(triphenylphosphine)rhodium(I) and related rhodium[13] and iridium[14] complexes. One formulation of this hypothesis is outlined in eq 1–3.







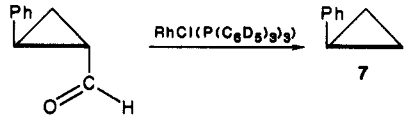
The sequences of steps leading to and from the unsaturated intermediate RhClL$_2$(COR)H in eq 1 and 3 are standard components of current mechanistic descriptions of the decarbonylation process.[15] If there were reductive elimination of an acyl chloride from the unsaturated intermediate,[16] followed by a phosphine association step and reversible orthometalation of hydridotris(triphenylphosphine)rhodium(I) (eq 2), then RCD=O and catalyst could lead to RCH=O and RhCl(PPh$_3$) labeled with deuterium at the ortho position of one phenyl ring, with subsequent decarbonylation of RCH=O, giving product with overall deuterium loss.

To test this hypothesis, deuterioaldehyde **8** was decarbonylated with RhClP(C$_6$D$_5$)$_3$)$_3$.[17]. The phenylcyclopropane obtained retained 87% of its deuterium label—a result noticeably higher than observed in previous runs with unlabeled Wilkinson's catalyst but also well below the 100% figure which the orthometalation hypothesis would predict. More tellingly, decarbonylation of undeuteriated *trans*-2-phenylcyclopropanecarboxaldehyde with d_{45} Wilkinson's catalyst gave *no* deuterium in the phenylcyclopropane product. The orthometalation conjecture thus failed, and an alternative rationale was sought.

Table I. RhCl(PPh$_3$)$_3$ Decarbonylations of Aldehydes 6 and 8 in Presence of Ethanol and Deuterium-Labeled Ethanols

entry	aldehyde	ethanol	equiv	product **7** + **9**, % d_0	recovd **6** + **8**, % d_0
1	**8**			74	43–49[a]
2	**8**	d_0	1	66	
3	**8**	d_0	4	86	94
4	**8**	d_0	10	94	54
5	**8**	d_0	10	93	80
6	**8**	d_0	12	94	80
7	**8**	d_6	11	32	18
8	**8**	d_1[b]	11	29	
9	**6**	d_6	9	42	20
10	**6**	d_1[b]	9	48	
11	**6**	d_2[c]	9	100	

[a] Four runs. [b] CH$_3$CH$_2$OD. [c] CH$_3$CD$_2$OH.



6 **7**

Wilkinson's catalyst is typically obtained through reaction of RhCl$_3$·3H$_2$O with PPh$_3$ in ethanol:[18] the product precipitates from the reaction mixture and is used without recrystallization. It may be, we speculated, that some ethanol is retained in the crystalline catalyst as usually prepared and that this ethanol might lead to loss of deuterium label.

Decarbonylation of deuterioaldehyde with Wilkinson's catalyst and added ethanol gave more complete loss of deuterium label in the product and loss of label in recovered aldehyde. Deuterioaldehyde and added CD$_3$CD$_2$OD gave decarbonylation product and recovered aldehyde having more deuterium label than observed when no ethanol was present. Added CH$_3$CD$_2$OH behaved like CH$_3$CH$_2$OH: there was no apparent involvement of C(1)D in exchange reactions. Table I sumarizes experiments with added ethanol and deuterium-labeled ethanols.

Even 11 equiv of CH$_3$CH$_2$OD or CD$_3$CD$_2$OD does not prevent extensive loss of label during the reaction **8** → **7** + **9** (Table I). Ethanol associated with the catalyst might contribute to decarbonylation product with loss of label more efficiently than deliberately added *O*-deuterioethanol through relatively slow exchange between coordinated and free ethanol molecules or through a kinetic isotope effect favoring the rate-determining oxidative addition of unlabeled aldehyde rather than deuterioaldehyde to RhClL$_2$.

Other experimental evidence, however, disproved the "ethanol hypothesis" conclusively. The ^{1}H NMR of commercial samples of Wilkinson's catalyst dissolved in CDCl$_3$ showed no trace of absorptions due to ethanol but did reveal a broad singlet at 1.8 ppm assignable to water associated with rhodium. Ths signal grew in intensity when water has deliberately added or could be removed by adding D$_2$O. Decarbonylation of deuterioaldehyde **8** run with Wilkinson's catalyst prepared in situ from [ClRh(C$_2$H$_4$)$_2$]$_2$ and PPh$_3$ in toluene,[19] and thus assuredly in the

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[15] Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640–641. Milstein, D. *Organometallics* **1982**, *1*, 1549–1551. Kampmeier, J. A.; Harris, S. H.; Mergelsberg, I. *J. Org. Chem.* **1984**, *49*, 621–625 and references cited therein.

[16] Compare Kampmeier, J. A.; Rodehorst, R. M.; Philip, J. B., Jr. *J. Am. Chem. Soc.* **1981**, *103*, 1847–1849. Kampmeier, J. A.; Mahalingam, S. *Abstracts of Papers*, 185th National Meeting of the American Chemical Society, Seattle, WA; American Chemical Society: Washington, DC, 1983; ORGN 32.

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[18] Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A.* **1966**, 1711–1732. Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67–81.

[19] Stern, R.; Chevallier, Y.; Sajus, L. *C. R. Seances Acad. Sci., Ser. C* **1967**, 1740–1742.

absence of ethanol, occurred with partial loss of label; decarbonylation of 8 with $ClRh(dppp)_2$,[20] another ethanol-free catalyst, likewise gave some d_0 product. Both spectroscopic and chemical findings, then, excluded ethanol as hydrogen source and reintroduced water as the probable alternative.

Reconsideration of the early experiment with d_0 aldehyde 6 and 1 equiv of D_2O, in light of the data summarized in Table I, suggested that it may have been misleading: relatively small percentages of deuterium incorportaion in the decarbonylation product would not have been detected by the analytical method then used, NMR spectroscopy, and substantial kinetic isotope effects could have favored formation of d_0 product from d_0 aldehyde.

This possibility was confirmed by running decarbonylations of deuterioaldehyde 8 in the presence of excess D_2O: the phenylcyclopropane obtained was 96–100% d_1 (four runs), while a control run without added D_2O gave a 58:42 mixture of 7 (d_0) and 9 (d_1).

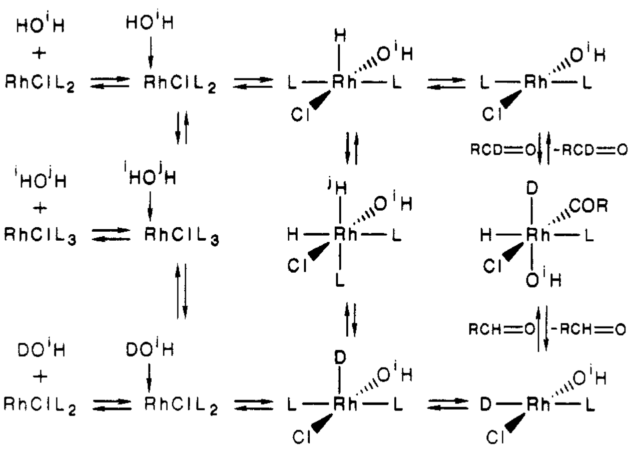
Discussion

Wilkinson's catalyst as usually prepared and isolated[18] contains some water, a happenstance that does not usually detract from applications to decarbonylation reactions but does lead to partial loss of deuterium label when deuterioaldehydes are substrates. Discordant results on decarbonylations of deuterioaldehydes may be associated with some substrate variability in sensitivity to the reactions responsible for the deuterium loss or with samples of Wilkinson's catalyst having different amounts of water associated with the crystalline complex or with solvents containing more or less water. Observation of less deuterium loss with the $RhCl(PPh_3)$-d_{45} catalyst prepared from PPh_3-d_{15} and $RhCl_3$ during decarbonylation of 8, together with lack of deuterium incorporation from a parallel decarbonylation of aldehyde 6, stimulated recognition that even a perdeuteriated version of Wilkinson's catalyst could be a source of hydrogen—if it were associated with some water present in the synthesis of the complex—and that different preparations and solvents could contain different amounts of water. Since $RhCl(PPh_3)_3$ (d_8, four-coordinate) is coordinatively unsaturated, water could well be associated with an otherwise vacant coordination site and be quite resistant to dissociation through for instance exposure to vacuum.

Perhaps water associated with $RhCl(PPh_3)_3$ also contributed to early reports[21] based on dilute solutions of the complex and vapor pressure osmometry that the complex had a low solution molecular weight, a conclusion later shown not to be due to extensive dissociation of triphenylphosphine.[22]

A formal mechanism to account for loss of deuterium label during decarbonylation of a deuterioaldehyde is shown in Scheme I. Loss of label is evident experimentally in both hydrocarbon product and recovered aldehyde; exchange of the aldehydic deuterium (Scheme I)[23] and normal decarbonylation (eq 1 and 3) will thus rationalize the observations most efficiently. Addition of aldehyde to RhClHL(OH), a 14e complex, may give a six-coordinate 16e species which could account for exchange of hydrogen between aldehyde and water (Scheme I); addition of aldehyde to $RhClL_2$, a 14e intermediate, gives a five-coordinate 16e product through oxidative addition on the route to decarbonylation (eq 1 and 3). These additions have some parallels, but the former gives a six-coordinate complex which cannot suffer migratory insertion.

Scheme I



L = PPh_3; 'H, 'H = H or D

This investigation provides a rational explanation for the originally baffling observation 1 → 2, one that is consistent with a variety of additional experimental tests. This explanation may offer clues to other seemingly abstruse chemistry observed in Wilkinson's catalyst promoted reactions, but more immediately and practically, it plainly specifies how to avoid loss of deuterium label during decarbonylations of deuterioaldehydes.

Experimental Section

Analytical gas chromatographic work was done by using 0.2-mm i.d. 25-m cross-linked dimethyl silicone and phenyl methyl silicone fused silica capillary columns, a Hewlett-Packard 5790 instrument with both columns connected to a single injection port, and the two FID detectors connected to HP 3390A and 3392A reporting integrators. Preparative gas chromatographic separations were done on packed columns[10] by using Varian Aerograph A90-P3 or 1520 instruments. Proton NMR spectra were measured on Varian T-60 or XL-100 or on a General Electric QE-300 spectrometer; chemical shifts were measured in ppm for $CDCl_3$ solutions relative to Me_4Si ($\delta = 0.0$) as internal standard. Mass spectra were obtained with a Hewlett-Packard 5970B mass selective detector interfaced to a 5890 series gas chromatograph and a 9336 computer. Ethanol-d_6, O-deuterioethanol, and cycloheptane were obtained from Aldrich.

***trans*-2-Phenylcyclopropanecarboxaldehyde (6)** and the deuteriated analogues 1 and 8 were prepared and characterized as detailed in published work.[10]

Phenylcyclopropane (7) and *trans*-1-deuterio-2-phenylcyclopropane (8), required as standards for mass spectroscopic analyses, were prepared as described in earlier work.[10]

Cycloheptanedeuteriocarboxaldehyde[24] (10) was obtained in two steps from cycloheptanecarboxylic acid through reduction with lithium aluminum deuteride followed by oxidation using pyridinium chlorochromate in CH_2Cl_2. The aldehyde obtained was purified by preparative gas chromatography using a QF1 column: ^{1}H NMR 1.0–3.1 ppm (m).

Cycloheptane-d_1 (12) was prepared from cycloheptanol by way of the tosylate;[25] reduction of cycloheptyl tosylate with lithium

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Table II. Mass Spectrometric Ion Intensity Ratios for Reference Unlabeled and Monodeuterio Compounds

compd	$((M + 1)/M)d_0$	$(M/(M + 1))d_1$	M
11	0.072[a]		98
12		0.0[a]	98
7	0.086		118
9		1.810	118
6	0.064		146
8		1.509	146

[a] Determined in scan mode; other ratios in single-ion monitoring mode.

aluminum deuteride in ether, followed by a standard workup, gave the $C_7H_{13}D$ product. By capillary GC on two different columns it was indistinguishable from authentic cycloheptane (Aldrich): mass spectrum, *m/e* 99 (M^+, 60% of base peak at *m/e* 56).

Wilkinson's catalyst-d_{45} was prepared following the detailed literature precedent.[17] Benzene-d_6 (Aldrich, 99+ atom % D) was brominated; bromobenzene-d_5 was converted to the corresponding Grignard reagent, which was combined with PCl_3 to afford $P(C_6D_5)_3$. Triphenylphosphine-d_{15} and $RhCl_3{\cdot}3H_2O$ in ethanol gave the desired perdeuteriated catalyst as a brick-red crystalline material, mp 137 °C with decomposition (d_0 complex, lit.[21] mp 138 °C dec; lit.[18] mp 157–158 °C).

Ethanol-*1,1*-d_2 was prepared by reducing acetyl chloride with $LiAlD_4$ in bis(2-ethoxyethyl) ether.[26] Following workup, the alcohol was secured as 95% CH_3CD_2OH/5% H_2O by distillation at atmospheric pressure.

Decarbonylation of Aldehydes. A solution of aldehyde, freshly purified by preparative GC, and degassed benzene was added to a reaction vessel containing a magnetic stirring bar and 1 equiv of Wilkinson's catalyst. An argon atmosphere was established and the reaction mixture was suspended in an oil bath at 83 °C. Following the decarbonylation reaction, pentane was added, and the pentane/reaction mixture combination was filtered through a short column containing a fixed amount of silica. The eluted material was analyzed by capillary gas chromatography and by GC/MS.

Mass spectral analyses to determine content for cycloheptane, phenylcyclopropane, and *trans*-2-phenylcyclopropanecarboxaldehyde samples were based on the relative intensities of *m/e* M and M + 1 signals and the appropriate equation[26] relating the observed (M + 1)/M ratio for a sample of unknown deuterium content to d_0/d_1 (eq 4).

$$\frac{d_0}{d_1} = \left[\left(\frac{M+1}{M}\right)\left(\frac{M}{M+1}\right)_{d_1} - 1\right] \Big/ \left[\left(\frac{M+1}{M}\right)_{d_0} - \left(\frac{M+1}{M}\right)\right] \quad (4)$$

Here d_0 and d_1 as subscripts refer to ion ratios determined with authentic d_0 and d_1 reference compounds. This approach makes no allowance for less than 100% incorporation of deuterium in authentic d_1 molecules nor for natural abundance deuterium in d_0 reference molecules. Both errors are taken to be small and of negligible consequence for the major concerns of this study.

Ion ratios determined for reference compounds are summarized in Table II.

^1H NMR Spectrum of Commercial Wilkinson's Catalyst. Solutions of $RhCl(PPh_3)_3$ from either Strem or Aldrich in $CDCl_3$ gave ^1H NMR spectra showing no hint of absorptions from contamination by ethanol and no absorptions in the 0 to −18 ppm region (392 scans at a sweep width of 7000 Hz). A relatively weak broad singlet at 1.8 ppm was evident; it increased in intensity when H_2O was added. Solutions of catalyst treated with D_2O showed a decrease and in time a complete loss of this absorption.

Wilkinson's catalyst from Strem also showed a small sharp singlet at 1.27 ppm, which did not disappear when D_2O was added. Catalyst from Aldrich also showed this weak absorption.

Decarbonylation of Aldehyde 8 with Wilkinson's Catalyst from Chlorobis(ethene)rhodium(I) Dimer. To an oven-dried 5-mL vial fitted with magnetic stirring bar were added under argon 24 mg (6.2×10^{-5} mol) of $[ClRh(C_2H_4)_2]_2$, 95 mg (36×10^{-5} mol) of triphenylphosphine, and 1 mL of toluene, freshly distilled from CaH_2.[19] The vial was sealed with a screw-on septum cap under argon, and a needle connected through an adapter to an oil bubbler was inserted. When the evolution of ethylene subsided, after 3 min, 20 mg (1.4×10^{-4} mol) of deuterioaldehyde 8 was injected into the vial. After being kept at 80 °C for 5 h, the reaction mixture was examined by GC/MS: the phenylcyclopropane product was 43% d_0 (7), 57% d_1 (9), as determined by GC/MS analysis.

Decarbonylation of Aldehyde 8 with Chlorobis[1,3-bis(diphenylphosphino)propane]rhodium(I). To a two-necked distillation flask were added 5.4 mg (7.8×10^{-6} mol) of $ClRh(CO)(PPh_3)_3$, 9.2 mg (2.2×10^{-5} mol) of 1,3-bis(diphenylphosphino)propane, 10 mL of xylene, and a magnetic stirring bar.[20] One neck was fitted with a septum and the other with a Soxhlet extractor containing 3A molecular sieves. The flask was heated to reflux for 3 h, and then 10 mg (6.8×10^{-5} mol) of deuterioaldehyde 8 was injected. Decarbonylation was allowed to proceed overnight at reflux: the product phenylcyclopropane according to analysis by GC/MS was obtained as a 66:34 mixture of **7** (d_0) and **9** (d_1).

Decarbonylation of Aldehyde 8 with Wilkinson's Catalyst in the Presence of D_2O. Toluene (0.25 mL), Wilkinson's catalyst (Strem; 53 mg, 5.7×10^{-5} mol), 12.5 mg (6.9×10^{-4} mol) of D_2O, and 12.6 mg (8.6×10^{-5} mol) of deuterioaldehyde 8 were added to a dry 5-mL vial under argon. The reaction mixture was heated at 80 °C for 5 h, cooled, and diluted with 1 mL of pentane; filtration of the pentane–toluene solution through a short column of silica was followed by GC/MS analysis of the filtrate. The product phenylcyclopropane was found to be 4% d_0 (7) and 96% d_1 (9).

Three repetitions of this experiment led to phenylcyclopropane that was 97%, 100%, and 96% d_1. A control experiment run in an identical fashion but without added D_2O gave a 58:42 mixture of d_0/d_1 products (7/9).

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