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Mechanism of Rearrangement of Platinacyclobutanes

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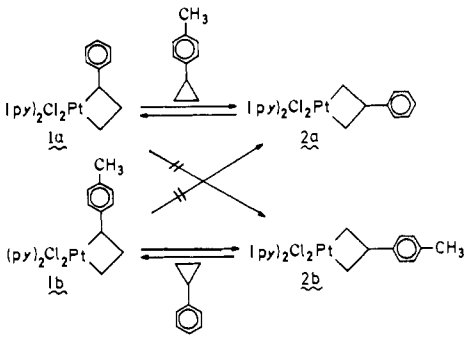
Abstract: No crossover products were observed when the rearrangement of dichlorobis(pyridine)(1-phenylpropane-1,3-diyl)-platinum(IV) (**1a**) to dichlorobis(pyridine)(2-phenylpropane-1,3-diyl)platinum(IV) (**2a**) was carried out in the presence of either *p*-tolylcyclopropane or *p*-methylstyrene. Preparation of dichlorobis(pyridine)(*cis*-1-phenylpropane-3-d_1-1,3-diyl)platinum(IV) (**5a**) from *cis*-phenylcyclopropane-2-d_1 and rearrangement of **5a** to the β-phenylplatinacyclobutane **6** both proceeded with complete retention of stereochemistry.

The olefin metathesis reaction[1] has been proposed to proceed via interconversion of metal–alkene–carbene complexes and metallacyclobutanes.[2] This proposal is supported both by studies of the reactions of metal carbene complexes with alkenes[3] and by labeling experiments which show that the olefin metathesis reaction proceeds in a nonpairwise manner.[4] Our interest in the metathesis reaction has led us to study the rearrangement of platinacyclobutanes which was first discovered by Puddephatt.[5] Puddephatt found that the initially formed α-phenylplatinacyclobutane **1a** formed by ring opening of phenylcyclopropane rearranges to a mixture of α- and β-phenylplatinacyclobutanes **1a** and **2a** on heating. Initially it seemed possible that this rearrangement proceeded by a mechanism closely related to that proposed for olefin metathesis. Here we present the results of mechanistic studies of the rearrangement of platinacyclobutanes.

Results

The possibility that the rearrangement of the α-phenylplatinacyclobutane **1a** to the β-phenyl isomer **2a** proceeded via elimination and readdition of phenylcyclopropane was seriously considered since thermal decomposition of **1a** or **2a** gives some phenylcyclopropane[5,6] and since reaction of **1a** or **2a** with $P(C_6H_5)_3$ gives a high yield of phenylcyclopropane.[7] Rearrangement of **1a** to a 1:2 equilibrium mixture of **1a:2a** in the presence of *p*-tolylcyclopropane led to no formation of α- or β-(*p*-tolyl)platinacyclobutanes **1b** or **2b.** Similarly, rearrangement of α-(*p*-tolyl)platinacyclobutane **1b** in the presence of phenylcyclopropane gave a 1:4 equilibrium mixture of **1b:2b** and no phenylplatinacyclobutanes **1a** or **2a.**



Heating a mixture of dichlorobis(pyridine)(1-hexylpropane-1,3-diyl)platinum(IV) (**1c**) and the corresponding 2-hexyl derivative, **2c**, in the presence of phenylcyclopropane at 50 °C for several hours gave no **1a** or **1b.** Puddephatt has reported that the rearrangement of alkyl-substituted platinacyclobutanes is substantially faster than that of aryl-substituted platinacyclobutanes.[8] Our experiment helps establish that coordination of the phenyl ring to platinum is not the means of maintaining the intramolecularity of the rearrangement.

The possibility that the rearrangement of **1a** to **2a** proceeded by fragmentation to styrene and a $Pt{=}CH_2$ species was

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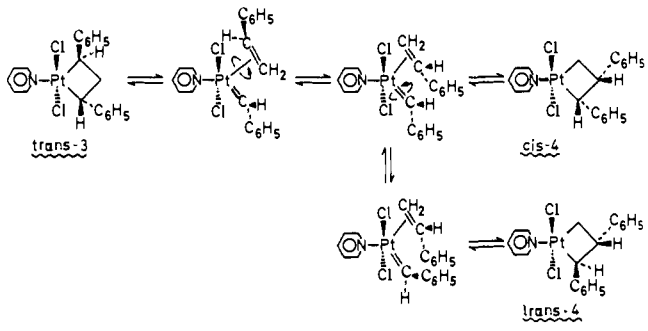
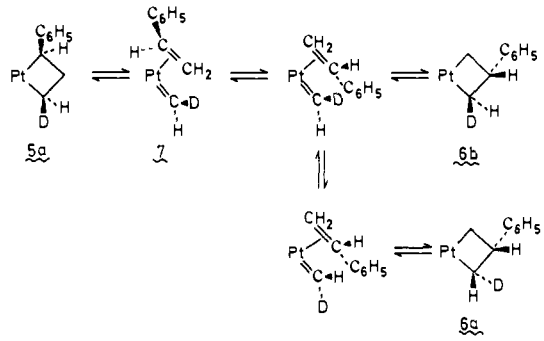
Scheme I



Scheme II



eliminated by a similar crossover experiment. Rearrangement of **1a** in the presence of *p*-methylstyrene led to an equilibrium mixture of **1a** and **2a**; no *p*-tolylplatinacyclobutane **1b** or **2b** was observed.

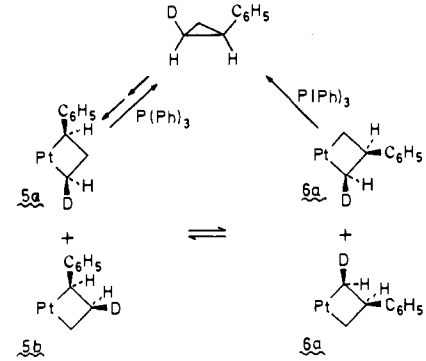
Puddephatt has reported that the *trans*-2,4-diphenylplatinacyclobutane, *trans*-**3**, obtained from *trans*-1,2-diphenylcyclopropane rearranges to a *trans*-2,3-diphenylplatinacyclobutane, *trans*-**4**.[9] The formation of only *trans*-**4** might be due to either a stereospecific rearrangement or to the initial formation of a *cis*-2,3-diphenylplatinacyclobutane, *cis*-**4**, followed by isomerization to give the more stable *trans*-**4**. Puddephatt has noted that models of *cis*- and *trans*-**4** indicate great steric crowding in the cis isomer.[9] Equilibration of *cis*-**4** and *trans*-**4** could have resulted from rearrangement via a metal-carbene-alkene complex as shown in Scheme I. Unfortunately, platinacyclobutanes could not be prepared from *cis*-1,2-diphenylcyclopropane (or other cis-disubstituted cyclopropanes).[9,10] This precluded studies of the stereochemistry of the platinacyclobutane rearrangement starting with *cis*-**3**.

To determine the stereochemistry of the platinacyclobutane rearrangement we have examined the rearrangement of *cis*-2-phenyl-4-deuterioplatinacyclobutane (**5a**) to its 3-phenyl isomer **6**. If the reaction proceeds through metal-carbene-alkene complex **7** shown in Scheme II, rotation of the alkene ligand which is required for rearrangement would place the phenyl and deuterium substituents in a trans orientation, **6b**. If rotation of the carbene ligand also occurs then some cis-phenyl, deuterium-substituted material, **6a**, would also be obtained. The key point is that some loss of stereochemistry would be expected to accompany a reaction proceeding through metal-carbene-alkene complex **7**.

Reaction of *cis*-phenylcyclopropane-2-d_1 with $[(CH_2{=}CH_2)PtCl_2]_2$ followed by treatment with pyridine gave deuterated α-phenylplatinacyclobutane (**5a, 5b**). The cis stereochemical relationship between phenyl and deuterium in **5a** and **5b** was demonstrated by reaction with triphenylphosphine,[7] which produced $Pt[P(C_6H_5)_3]_2Cl_2$ and *cis*-phenylcyclopropane-2-d_1.

The 270-MHz ^1H NMR spectrum of phenylcyclopropane shows clearly separated multiplets at δ 0.88 due to trans hydrogens and δ 0.64 due to cis hydrogens. Integration of the 270-MHz spectrum of the *cis*-phenylcyclopropane-2-d_1 used to prepare **5a** and **5b** gave a cis:trans ratio of 1.02 ± 0.03:2.0, indicating that all (98 ± 3%) of the deuterium is cis to the phenyl. Integration of the ^1H NMR spectrum of deuterated phenylcyclopropane recovered from $P(C_6H_5)_3$ treatment of the **5a** and **5b** mixture gave a cis:trans ratio of 1.00 ± 0.03:2.0, indicating that within experimental error no loss of stereochemistry had occurred. Rearrangement of deuterated α-phenylplatinacyclobutane (**5a** and **5b**) to an equilibrium mixture of 1:2 α-:β-phenylplatinacyclobutanes **6** was accomplished by heating to 50 °C for 15 h in $CDCl_3$. The mixture of isomers was treated with $P(C_6H_5)_3$ to give $Pt[P(C_6H_5)_3]_2Cl_2$ and phenylcyclopropane. Analysis of the phenylcyclopropane by 270-MHz ^1H NMR demonstrated that all (98 ± 3%) of the deuterium label was cis to the phenyl group.

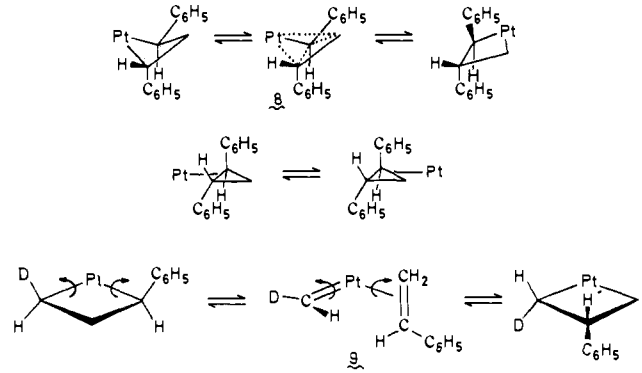
In addition, the ^2H NMR spectrum of the deuterated cyclopropane recovered from the equilibrium mixture of platinacyclobutanes **5** and **6** gave a single peak due to a deuterium cis to the phenyl group; the amount of deuterium trans to phenyl was ≤10%. The ^2H NMR spectrum of a mixture of cis- and trans-deuterated phenylcyclopropanes, prepared by reaction of an isomeric mixture of 2-bromophenylcyclopropanes with *n*-butyllithium followed by D_2O, gave two well-resolved resonances for the cis and trans deuterium atoms. Thus the platinacyclobutane rearrangement proceeds with complete retention of stereochemistry. This result rules out the mechanism shown in Scheme II.



Discussion

The observed retention of stereochemistry in the rearrangement of *trans*-**3** to *trans*-**4** and of **5a** to **6a** can be explained with Puddephatt's postulate of a concerted rearrangement as depicted in transition state **8**.[5] Alternatively, the rearrangement can be thought of as arising from formation of an edge-metalated cyclopropane which then undergoes an edge to edge isomerization and ring opening.

A way of looking at the rearrangement which is closely related to Puddephatt's proposal of **8** is to consider the defor-



mation of a planar metallacyclobutane through a puckered metallacyclobutane and on to a complex in which the plane of the alkene and the plane of the carbene ligand become perpendicular as in **9.** This is accomplished by rotating the incipient carbene ligand by 90° while at the same time rotating the incipient alkene ligand by 90° in the opposite direction. Concerted rotation of the two ligands can lead back to starting material or to isomerized product with retention of stereochemistry. Whether **9** is an intermediate or a transition state is uncertain. If **9** is an intermediate, then independent rotation of either the carbene or the alkene ligand must have a substantial barrier while concerted rotation of both ligands in opposite senses must have a very low activation barrier. One reason that concerted rotation may be favored is that this motion leads smoothly (via a bonding interaction between the carbene ligand and one end of the alkene) to the metallacyclobutane.

Experimental Section

Phenylacetylene-d_1. Phenylacetylene (45 g, 0.44 mol) and 25 mL of D_2O containing 0.1 g of BaO were stirred for 2 days. The phenylacetylene was separated and three additional exchanges with D_2O were carried out in an identical fashion. Distillation gave phenylacetylene-d_1 [30 g, 66% recovery, bp 35–40 °C (15 mm), <2% d_0 material by ^{1}H NMR].

***cis*-1-Phenyl-2,2-dichlorocyclopropane-*3*-d_1.** A solution of diisobutylaluminum hydride in hexane (320 mL, 1.0 M, 0.32 mol) was added to phenylacetylene-d_1 (30 g, 0.29 mol) in 75 mL of hexane at 0 °C under a N_2 atmosphere. The mixture was heated to 50 °C for 2.5 h and then hydrolyzed at 0 °C with 120 mL of 25% aqueous H_2SO_4. The organic layer and pentane extract were dried ($CaCl_2$) and distilled to give styrene [19.8 g, bp 37 °C (14 mm)]. ^{1}H NMR of the styrene indicated it to be an 80:15:5 mixture of *cis*-β-deuteriostyrene (<2% styrene-d_0)–phenylacetylene–ethylbenzene.

Chloroform (37.7 g), 30 mL of 50% aqueous NaOH, 0.5 g of benzyltriethylammonium chloride, and 11.8 g of the mixture containing *cis*-β-deuteriostyrene were stirred for 4 h at 40–50 °C and then diluted with H_2O and CH_2Cl_2.[11] Vacuum distillation gave *cis*-1-phenyl-2,2-dichlorocyclopropane-*3*-d_1 [8.94 g, 28% yield from phenylacetylene-d_1, bp 70 °C (0.5 mm); NMR ($CDCl_3$) δ 7.2–7.3 (5 H, m), 2.87 (1 H, d, J = 10.7 Hz), and 1.91 (1 H, d, J = 10.7 Hz); exact mass 187.0066 (calcd for $C_9H_7DCl_2$, 187.0066).

***cis*-Phenylcyclopropane-*2*-d_1** was prepared by the method of Dale and Swartzentruber.[12] Small pieces of sodium (6.7 g, 0.29 mol) and a mixture of 45 mL of CH_3OH containing 1.5 mL of H_2O were added in portions over 1.5 h to a solution of *cis*-1-phenyl-2,2-dichlorocyclopropane-*3*-d_1 (2.73 g, 14.5 mmol) in 15 mL of ether at 0 °C. After the solution was stirred overnight at room temperature, 40 mL of water was added, and the aqueous layer was acidified with HCl and extracted twice with ether. The combined organic layers were dried ($MgSO_4$) and distilled to give *cis*-phenylcyclopropane-*2*-d_1 [bp 62 °C (14 mm), lit.[12] bp 69 °C (12 mm), 0.78 g, 46%]. NMR ($CDCl_3$): δ 7.3–6.9 (5 H, m), 1.84 (1 H, t of d, J = 8.4, 5.0 Hz), 0.88 (2 H, m), 0.64 (1 H, m). Integration of the 270-MHz ^{1}H NMR spectrum indicated that the ratio of hydrogens cis to phenyl (δ 0.64) to hydrogens trans to phenyl (δ 0.88) was 1.02 ± 0.03:2.0.

Phenylcyclopropane, bp 170 °C (lit.[13] bp 169–171 °C), *p*-tolylcyclopropane, bp 79–82 °C (14 mm) [lit.[14] bp 79–80 °C (14 mm)], and *n*-hexylcyclopropane, bp 150 °C (lit.[15] bp 148 °C), were prepared similarly by phase-transfer-catalyzed :CCl_2 addition to the corresponding olefin, followed by sodium–methanol reduction.

Dichlorobis(pyridine)(*cis*-1-phenylpropane-*3*-d_1-1,3-diyl)platinum (5a) and Dichlorobis(pyridine)(*cis*-1-phenylpropane-*2*-d_1-1,3-diyl)platinum (5b). A mixture of $[PtCl_2(C_2H_4)]_2$ (100 mg, 0.17 mmol) and *cis*-phenylcyclopropane-*2*-d_1 (0.21 g, 1.8 mmol) was refluxed in ether for 5 h. The resulting light yellow precipitate was collected by filtration, washed with ether, and dried under vacuum. The resulting tetrameric platinum cyclopropane complex was suspended in 3 mL of CH_2Cl_2 and 0.12 mL of pyridine was added. After stirring for a few minutes the solution was filtered, solvent was evaporated, and the residual yellow solid was washed thoroughly with hexane and dried under vacuum to give **5a** and **5b** (115 mg, 62%), mp 130–135 °C. The ^{1}H NMR spectrum showed the benzylic proton at δ 4.93 as an overlapping doublet due to **5b**, J = 9 Hz, and triplet due to **5a**, J = 9 Hz, with Pt satellites, $J_{^{195}Pt-H}$ = 102 Hz. Complex multiplets at δ 8.9–6.9 due to aromatic hydrogens and at δ 3.4–2.4 due to the remaining ring hydrogens were observed.

Platinacyclobutanes **1a, 1b,** and **1c** were prepared in the same manner as previously reported.[5,10,16]

Cyclopropane Crossover Experiments. A mixture of **1a** (71 mg, 0.13 mmol) and *p*-tolylcyclopropane (87 mg, 0.65 mmol) was sealed in a glass tube in $CHCl_3$. The tube was heated to 52 ± 1 °C for 21 h. The tube was then opened, volatile components were pumped off, and the Pt complex was washed with pentane and pumped on under high vacuum to remove the last traces of free cyclopropane. The NMR spectrum of the recovered complex showed an equilibrium mixture of α- and β-phenylplatinacyclobutanes, and no aromatic methyl resonance, indicating that only **1a** and **2a,** and no **1b** or **2b,** were present.

A $CHCl_3$ solution of **1b** (88 mg, 0.16 mmol) and phenylcyclopropane (94 mg, 0.80 mmol) was heated to 52 °C for 22 h, and the platinum complex was isolated as above. The NMR spectrum showed a 1:4 mixture of α- and β-*p*-tolylplatinacyclobutanes with no evidence for formation of **1a** or **2a.**

A $CDCl_3$ solution of **2c** and **1c** (46 mg, 0.084 mmol) and phenylcyclopropane (19 mg, 0.16 mmol) was heated to 50 °C and NMR spectra were run after 2.5 and 6.5 h. Gradual decomposition of the platinum complex took place, but no formation of **1a** or **2a,** which would have given rise to characteristic benzylic proton multiplets at δ 4.9 and 4.05, was visible.

***p*-Methylstyrene Crossover Experiment.** A $CDCl_3$ solution of **1a** (70 mg, 0.13 mmol) and *p*-methylstyrene (46 mg, 0.39 mmol) was heated to 53 °C for 15.5 h and the platinum complex was isolated as above. The NMR spectrum of the recovered complex showed an equilibrium mixture of isomers, along with some *p*-methylstyrene. There was no evidence for formation of **1b** or **2b.**

Reaction of Platinacyclobutanes with $P(C_6H_5)_3$. The mixture of **5a** and **5b** (44 mg, 0.081 mmol) was dissolved in chloroform and $P(C_6H_5)_3$ (44 mg, 0.17 mmol) was added. Reaction took place rapidly on shaking, forming a copious, white precipitate of $Pt[P(C_6H_5)_3]_2Cl_2$ which was separated from the solution by centrifugation and decantation. Pyridine and phenylcyclopropane were the only products observed by NMR, and no unreacted platinacyclobutane could be observed. Phenylcyclopropane was isolated by preparative GC (15% QF-1, Chromosorb P 60/80, 10 ft × 3/8 in., 115 °C). Analysis by 270-MHz ^{1}H NMR showed that no isomerization of the deuterium had taken place; the cis:trans ratio was 1.00 ± 0.03:2.0.

A mixture of **5a** and **5b** (92 g, 0.17 mmol) was sealed in a tube with $CDCl_3$, and the tube was heated to 50 °C for 15 h. The tube was then opened, and $P(C_6H_5)_3$ (92 mg, 0.35 mmol) in 0.5 mL of $CHCl_3$ was added. Reaction took place after shaking for a few minutes. The ^{1}H NMR spectrum showed only pyridine and phenylcyclopropane, and no unreacted platinacyclobutane. GC analysis (25% QF-1, Chromosorb P, 6 ft × 1/8 in., 91 °C) showed pyridine and phenylcyclopropane to be the only products; the yield of phenylcyclopropane by GC was 86%. The phenylcyclopropane was isolated as above. The 270-MHz ^{1}H NMR spectrum was identical with that of the original cyclopropane (cis:trans was 1.06 ± 0.03:2.0), indicating that no isomerization had taken place. Filtration gave $Pt[P(C_6H_5)_3]_2Cl_2$ (110 mg, 82%), mp 300–310 °C dec (lit.[17] mp 310 °C dec).

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Stereochemistry and Mechanism of the Reaction of $LiCu(CH_3)_2$ with β-Cyclopropyl α,β-Unsaturated Ketones

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Abstract: 1,6-Dimethylbicyclo[4.1.0]-4-hepten-3-one-*exo*-7-d_1 (**9**-d_1) was stereospecifically synthesized in seven steps from *o*-xylene. The reaction of $LiCu(CH_3)_2$ with **9**-d_1 gave a 48:52 mixture of the normal conjugate addition product *exo*-1,5,6-trimethylbicyclo[4.1.0]heptan-3-one-*exo*-7-d_1 (**19**-d_1) and of the cyclopropane ring opened product 5-(ethyl-*1*-d_1)-4,5-dimethyl-3-cyclohexenone (**12**-d_1). The stereochemistry of the ring-opened product **12**-d_1 was determined by 270-MHz ^1H NMR. The ratio of the diastereotopic methylene protons of the ethyl group of **12**-d_1, which appear at δ 1.48 and 1.33, was found to be 0.053 ± 0.02:1.0. The high stereospecificity of the ring-opening reaction provides evidence against radical anion intermediates in this reaction and is interpreted in terms of a direct nucleophilic attack of cuprate at the cyclopropyl carbon atom.

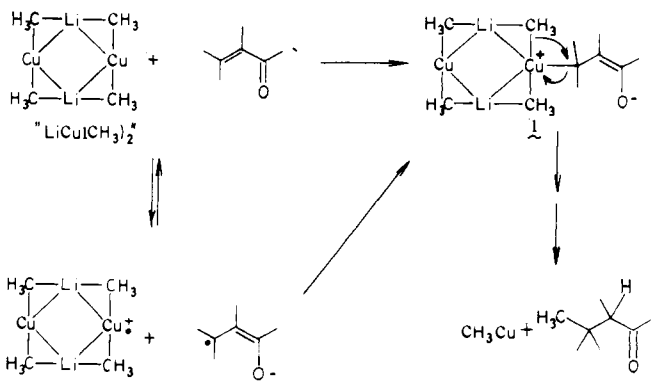
Introduction

While the conjugate addition of lithium diorganocuprates to α,β-unsaturated carbonyl compounds has proved to be extremely valuable in organic synthesis, its mechanism remains incompletely defined.[1] At one point, a six-centered transition state was considered, but this possibility was eliminated by the observation that lithium dimethylcuprate adds to *trans*-3-penten-2-one to give 69% of the trans enolate.[2] The absence of free radicals in the conjugate addition reaction has been demonstrated by several experiments: (1) reaction of lithium *tert*-butyl(*endo*-2-norbornyl)cuprate with mesityl oxide yields the conjugate adduct, 4-methyl-4-(*endo*-2-norbornyl)pentan-2-one, with no detectable exo isomer;[3] (2) reaction of either lithium di-*cis*- or di-*trans*-1-propenylcuprate with 2-cyclohexenone occurs with retention of stereochemistry at the propenyl group;[4] (3) isoprene does not interfere with the conjugate addition reactions of organocuprates.[5]

The conjugate addition of lithium dimethylcuprate, $LiCu(CH_3)_2$,[6] to unsaturated ketones is now thought to proceed either by an electron-transfer mechanism[7] or by a nucleophilic addition mechanism (Scheme I).[8] Both mechanisms are viewed as proceeding via an oxidative addition to give a Cu(III) adduct,[9] **1**, which subsequently undergoes reductive elimination of the observed enolate; however, there is no direct evidence for a Cu(III) intermediate, and direct transfer of an alkyl group cannot be excluded. The two mechanisms differ in the way in which the oxidative addition is accomplished. In the electron-transfer mechanism, $LiCu(CH_3)_2$ transfers an electron to the enone to produce the radical anion of the enone and a radical cation of the cuprate; subsequent combination produces **1**. Alternatively, $LiCu(CH_3)_2$ can act as a nucleophile and add to the β carbon of the enone without the intervention of odd-electron species.

The nucleophilic addition mechanism is similar to the familiar Michael addition reaction. The ability of organocuprates to act as nucleophiles has been demonstrated in substitution

Scheme I



reactions[10] with alkyl halides,[6a,11] tosylates,[8] and epoxides,[9a] all of which proceed with inversion of stereochemistry.

House has cited several experiments that support his proposed electron-transfer mechanism. First, the susceptibility of unsaturated carbonyl compounds to conjugate addition of organocuprates was found to correlate strongly with the one-electron polarographic reduction potentials of the unsaturated carbonyl compounds.[7,12] This implies that organocuprates can act as one-electron reducing agents;[13] however, one-electron electrochemical oxidation of organocuprates has not been observed polarographically.[7] Johnson has suggested that the reduction potential measures the affinity of the substrate for electrons and that correlation with either an electron-transfer process or a nucleophilic addition process might be expected.[8] In a rejoinder, House has pointed out that no obvious correlation exists between reduction potentials of unsaturated carbonyl compounds and their reactivity in the Michael reaction, and that steric effects of β-alkyl groups play a dominant role in the Michael reaction.[7a]

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