remained clear: ^{1}H NMR δ 7.7 (m (remainder of Ph signal obscured by toluene peak), Ph), 4.0 (d, J = 1 Hz, Cp), 3.12 (d, J = 16 Hz, NH), 2.44 (s, CH_3CO), 1.66 (t, $AlCH_2CH_3$), 0.95 (s, *t*-Bu), 0.45 (q, $AlCH_2CH_3$); ^{13}C NMR 323.8 (d, J = 29.0 Hz, $CH_3COAlEt_3$), 217.3 (d, J = 31.1 Hz, FeCO), 138.0 (d, J = 51.0 Hz), 136.5 (d, J = 52.9 Hz, Ph_{ipso}), 132.9 (d, J = 11.5 Hz), 131.0 (d, J = 10.8 Hz, Ph_{ortho}), 130.8 (d, J = 1.7 Hz), 130.2 (d, J = 1.3 Hz, Ph_{para}), 86.6 (s, Cp), 55.5 (d, J = 8.2 Hz, $C(CH_3)_3$), 50.8 (d, J = 3.0 Hz, $CH_3COAlEt_3$), 32.0 (d, J = 3.7 Hz, $C(CH_3)_3$); ^{31}P NMR 96.5 ppm.

X-ray Crystallographic Data. Large, well-shaped brownish black crystals of **5a**, obtained as described above, were sent to Molecular Structures Corp., College Station, TX, for analysis. A nearly spherical crystal of approximate diameter 0.40 mm was mounted in a glass capillary in a random orientation. Preliminary examination revealed the crystal to be triclinic, with cell parameters a = 10.474 (2) Å, b = 15.677 (3) Å, c = 9.707 (1) Å, α = 97.98 (1)°, β = 115.01 (1)°, γ = 71.81 (1)°, V = 1373.1 Å^3, Z = 2, and space group $P\bar{1}$.

Data were collected on an Enraf-Nonius CAD4 computer-controlled diffractometer, using graphite-monochromated Mo K$\bar{\alpha}$ radiation, at a temperature of 23 ± 1 °C. The ω–θ scan technique was used, with scan rates from 2 to 20°/min, to a maximum 2θ of 56.0°. A total of 6816 reflections were collected, of which 6602 were unique. As a check on stability, three representative reflections were monitored over time; these showed a loss of intensity over the course of data collection of 151 ± 7 counts/h; a linear decay correction was applied. Lorentz and polarization corrections were applied to the data; no absorption correction was made.

Structure Solution and Refinement. The structure was solved by direct methods. Using 350 reflections (minimum E of 1.45) and 4000 relationships, a total of 16 phase sets were produced. A total of 24 atoms were located from an E map prepared from the phase set with probability statistics: absolute figure of merit = 1.31, residual = 0.24, and psi zero = 1.200. The remaining atoms were located in succeeding difference Fourier syntheses. A disorder was noted in the region of atoms C27 and C28A. A twofold rotational disorder (about the Al–C27 bond) was assumed, with a 3:2 occupancy ratio for C28A and C28B, respectively. Hydrogen atoms were located, and their positions and isotropic thermal parameters were refined. The temperature factors for the *tert*-butyl and ethyl group hydrogens were fixed and not refined. The disordered hydrogen atoms were not located. The largest peaks in the final difference map were less than half as high as those that yielded C(28B) and were in the region of the ethyl group. The structure was refined in full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$.

The standard deviation on intensities, $\sigma(F_o^2)$, is defined as follows: $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, Lp is the Lorentz–polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to 0.050.

Scattering factors were taken from Cromer and Waber.[44] Anomalous dispersion effects were included in F_c;[45] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[44] Only the 4303 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 420 variable parameters and converged (largest parameter shift was 0.48 times its esd) with unweighted and weighted agreement factors of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.049$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.068$. The standard deviation of an observation of unit weight was 1.93. The highest peak in the final difference Fourier had a height of 0.93 e/Å with an estimated error based on ΔF of 0.08. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin\theta)/\lambda$, and various classes of indices showed no unusual trends.

Acknowledgment. We thank C. Schramm and V. Parziale for assistance with NMR studies.

Supplementary Material Available: Listings of thermal parameters (Table VI), complete bond lengths (Table VII) and angles (Table VIII), least-squares planes (Table IX), observed and calculated structure factor amplitudes (Table X), torsional angles (Table XI), and intermolecular contacts (Table XII) for compound **5a** (42 pages). Ordering information is given on any current masthead page.

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(44) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. 4.

(45) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781–782.

Preparation of Cyclometalladisiloxanes of the Type $\overline{\mathrm{M(SiMeROSi}}\mathrm{MeR)}$ (R = Phenyl and Benzyl) and the Catalyzed Redistribution of $(HRMeSi)_2O$[1]

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Received May 4, 1982

New cyclometalladisiloxanes, $L_n\overline{\mathrm{M(SiMeROSi}}\mathrm{MeR)}$ (R = C_6H_5, $C_6H_5CH_2$), have been prepared from the interation of disiloxanes $(HRMeSi)_2O$ with low-valent complexes. L_4Pt (L = Ph_3P) selectively reacts with the *RR* and *SS* enantiomers to give only the metallacycles with Ph groups on opposite sides of the ring. The formation of the benzyl analogue is not stereoselective; both cis and trans isomers form. The reactions of $L_2(CO)ClIr$ with $(HRMeSi)_2O$ yield two isomers when R = $C_6H_5CH_2$ and all three possible isomers when R = C_6H_5. These metallacycles are catalyst precursors in a reaction that causes extensive redistribution of groups on silicon via Me/H, Ph/H, Ph/Me, and SiO/R exchanges.

Introduction

Certain classes of organosilanes will undergo redistribution reactions of the type shown in eq 1 when treated

$$R_4Si + R'_4Si \rightarrow 2R_{4-n}R'_nSi \ (n = 1\text{–}4) \qquad (1)$$

with catalytic quantities of transition-metal complexes. In order for the redistribution reaction to occur at low temperatures, there must be at least one Si–H bond or an activated Si–Si bond if the catalyst is a typical low-valent complex, e.g., $L_2(CO)ClIr$, $L_2Pt(C_2H_4)$, or L_2PdCl_2 (L = Ph_3P unless otherwise stated).[1c]

Curtis and Greene observed that cyclometalladisiloxanes of type 1 were active as catalysts for the disproportionation

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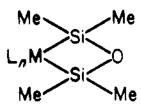
[1] This paper is part 6 in the series "Small Ring Metallacycles" and part 5 of "Metal-Catalyzed Redistributions of Organosilanes". For earlier papers, see: (a) Curtis, M. D.; Greene, J.; Butler, W. M. *J. Organomet. Chem.* **1979**, *164*, 371. (b) Curtis, M. D.; Greene, J. *J. Am. Chem. Soc.* **1978**, *100*, 6362. (c) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* **1981**, *19*, 213.

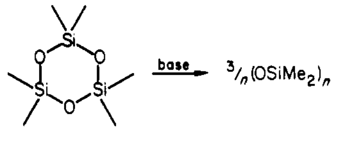


1a, $L_nM = L_2Pt$
b, $L_nM = L_2Pd$
c, $L_nM = L_2(CO)(H)Ir$

$$(n + 1)\underset{\text{E}'\text{E}'}{(\text{HMe}_2\text{Si})_2\text{O}} \rightarrow n\text{Me}_2\text{SiH}_2 + \underset{\text{E}'\text{D}_n\text{E}'}{\text{HMe}_2\text{Si}(\text{OSiMe}_2)_n\text{OSiMe}_2\text{H}} \quad (2)$$

of tetramethyldisiloxane, E′E′ (the short-hand notation is explained as follows: end group, E = $Me_3SiO_{1/2}$; difunctional, D = $Me_2SiO_{2/2}$; trifunctional, T = $MeSiO_{3/2}$. A primed symbol means hydrogen substituted for methyl: E′ = $HMe_2SiO_{1/2}$, D′ = $HMeSiO_{2/2}$, etc.; a superscript "P" means phenyl for methyl substitution, e.g., D^P = $PhMeSiO_{2/2}$, E'^P = $HPhMeSiO_{1/2}$. A superscript "B" means benzyl (Bz) for methyl substitution, e.g., E'^B = $HBzMeSiO_{1/2}$; and repetition of a symbol means multiple substitution, e.g., E'^{BB} = $HBz_2SiO_{1/2}$. Thus, $HMe_2SiOSiMe_2Ph$ ≡ $E'E^P$, $HMePhSiOSiMe_2OSiMe_3$ = E'^PDE, $(Me_3SiO)_2(HMe_2SiO)SiH$ = $E_2T'E'$, $E'^{PP}E$ = $HPh_2SiOSiMe_3$, etc.) according to eq 2. The reaction in eq 2 represents a route to polysiloxanes (silicones) fundamentally different from the usual hydrolysis method (eq 3) or the base-catalyzed ring-opening polymerization (eq 4). Therefore, new types of polysiloxanes might be made via metal-catalyzed disproportionation of 1,3-dihydridodisiloxanes.

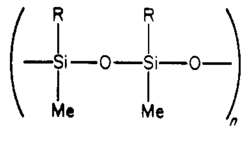
$$\text{Me}_2\text{SiCl}_2 + \text{H}_2\text{O} \rightarrow (1/n)(\text{OSiMe}_2)_n + 2\text{HCl} \quad (3)$$



(4)

D_3

We reasoned that stereoregular silicones, e.g., isotactic **2** or syndiotactic **3**, might form from disiloxanes such as $(HRMeSi)_2O$ (**4**). Disiloxanes **4** have two chiral centers and thus exist as the three stereoisomers **4a–c**. The belief that catalytic formation of polysiloxanes with metallacyclic catalysts might lead to stereoregular silicones was based on the fact that either **4a** or **4b** will react to give the trans metallacycle **5a**, but the *meso*-disiloxane **4c** can only produce the cis metallacycle **5b**.[2] Should these metallacycles have sufficiently different energies due to 1,3-cross-ring steric interactions, then one ring might form preferentially over the other. A difference of only about 3 kcal/mol in activation energies could give a 100:1 preference of **5a** over **5b**. Further reaction of the metallacycle according to a proposed mechanism[1] could then lead to stereoregular polysiloxanes.



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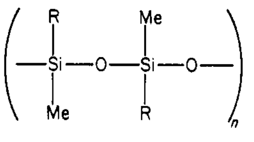

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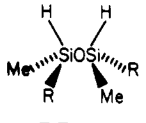
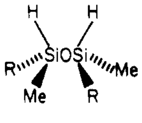
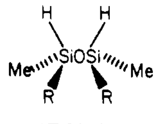


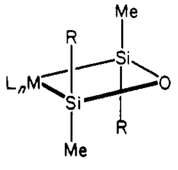
(*RR*)-**4a**



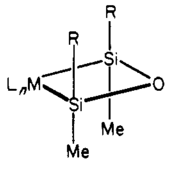
(*SS*)-**4b**



(*RS*)-**4c**



5a



5b

In this paper we report the synthesis of some new metallacycles, their use as catalysts for redistribution of $(HRMeSi)_2O$, and the metal–complex catalyzed redistribution reactions of some alkyl silanes.

Experimental Section

All manipulations were performed under an atmosphere of dry nitrogen using Schlenk ware techniques. Elemental analyses were carried out by Galbraith Laboratory, Knoxville, TN, and Spang Laboratory, Eagle Harbor, MI. Gas chromatographic analyses were performed on an Antek 300 gas chromatograph equipped with a thermal conductivity detector and a Hewlett-Packard 3380A integrator. Mass spectra were recorded on a Finnigan 4023 GC/MS instrument (ionizing voltage = 70 eV). Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. ^1H NMR spectra were recorded on a Varian A-60 or a JEOLCO JNM-PS-100 spectrometer or a Bruker 360-MHz spectrometer. The starting silanes and siloxanes were purchased from Petrarch Systems, Inc., and distilled prior to use. Vaska's ($L_2Ir(CO)Cl$) and Wilkinson's (L_3RhCl) complexes were prepared by literature procedures.[3,4] $L_2Pt(C_2H_4)$ was prepared by Malatesta's method.[5] Benzene was dried over potassium benzophenone and distilled under nitrogen. Bis(ethylene)(acetylacetonato)rhodium(I), $(acac)Rh(C_2H_4)_2$, was prepared by the method of Cramer.[6]

Benzylmethylchlorosilane (BzMeSiHCl) and Dibenzylmethylsilane. These compounds were prepared by a modified literature procedure.[7] An ethereal solution of benzylmagnesium chloride (300 mL, 0.35 M, 105 mmol) was added dropwise to an ice-cooled, three-neck flask containing 12.1 g (105 mmol) of methyldichlorosilane in ether. The flask was equipped with a mechanical stirrer, N_2 inlet, reflux condenser, and constant pressure dropping funnel. After the addition was complete, the white slurry was refluxed and stirred gently for 16 h. The mixture was then filtered under N_2 through a medium porosity frit, and the salts were washed with two 75-mL portions of ether. The ether was then distilled from the filtrate and the residue vacuum distilled to give two fractions: the major fraction, bp 55 °C (6 torr), is the desired BzMeSiHCl. The minor fraction, bp 95–96 °C (6 torr) is Bz_2MeSiH. For BzMeSiHCl: ^1H NMR (in C_2Cl_4) Ph δ 7.2 (m), HSi, 4.8 (sextet, J = 3 Hz) with each component showing further unresolved splitting, CH_3, 0.42 (d, J = 3 Hz) (all peaks in their correct area ratios 5:1:2:3, respectively); IR ν_{SiH} 2165, SiMe 1268 cm^{-1}; mass spectrum, m/e 170 (P^+), 155 ($P - Me^+$), 135 ($P - Cl^+$), 79 ($P - Bz^+$) (all with correct isotope patterns). Anal. Calcd for $C_8H_{11}ClSi$: C, 56.31; H, 6.45. Found: C, 56.41; H, 6.56.

For Bz_2MeSiH: ^1H NMR (in C_2Cl_4) Ph δ 7.5 (m), SiH 4.5 (octet, J = 3.6 Hz), CH_2 2.6 (d, J = 3.6 Hz), CH_3 0.5 (d, J = 3.6 Hz) (area ratios 1:4:3, respectively); IR (neat) ν_{SiH} 2120, SiMe 1265 cm^{-1}; mass spectrum, m/e 226 (P^+), 135 ($P - Bz^+$), 91 ($C_7H_7^+$).

1,3-Dibenzyl-1,3-dimethyldisiloxane. Benzylmethylchlorosilane (8.0 g, 47 mmol) was added dropwise to 20 mL of cold water, and then the mixture was stirred at room temperature for 2 h. The mixture was extracted with 3 × 20 mL portions of ether, and the extracts were dried over Na_2SO_4. Most of the ether was then distilled off at atmospheric pressure. Vacuum distillation of the residue gave the product as a colorless oily liquid: bp 109–110

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(2) This analysis assumes that the oxidative addition of L_nM into the Si–H bond proceeds with optical purity (all retention or all inversion) as has been shown for hydrosilation: Sommer, L. H.; Michael, K. W.; Fujimoto, H. *J. Am. Chem. Soc.* **1967**, *89*, 1519.

(3) Vrieze, K.; Collman, J. P.; Sears, C. T. *Inorg. Synth.* **1968**, *11*, 101.

(4) Osborne, J. A.; Jardin, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

(5) Malatesta, L.; Carriello, C. J. *J. Chem. Soc. A* **1958**, 2323.

(6) Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217.

(7) Jenkins, J. V.; Post, H. W. *J. Org. Chem.* **1950**, *158*, 552.

°C (5 torr); ^{1}H NMR (100 MHz in C_6D_6) Ph δ 7.3 (m), SiH δ 5.07 (sextet, J = 2.8 Hz), CH_2 2.26 (d, J = 2.8 Hz), CH_3 0.24 (d, J = 2.8 Hz); IR (neat) ν_{SiH} 2120, ν_{SiOSi} 1090–1030 (br, vs) SiMe 1265 cm^{-1}. Anal. Calcd for $C_{16}H_{22}OSi_2$: C, 67.13; H, 7.69. Found: C, 67.18; H, 7.71.

1,3-Diphenyl-1,3-dimethyldisiloxane. This disiloxane was prepared according to a literature method[8] by the hydrolysis of PhMeSiHCl (Petrarch Systems, bp 113 °C (100 torr)). The product is a colorless liquid: bp 96 °C (6 torr); ^{1}H NMR Ph δ 7.2 (m), SiH 5.15 (q, J = 2.8 Hz), Me 0.4 (d, J = 2.8 Hz); IR (neat) ν_{SiH} 2100, SiPh 1430, 1115; SiMe 1260, ν_{SiOSi} 1090–1030 cm^{-1} (br, vs). Anal. Calcd for $C_{14}H_{18}OSi_2$: C, 65.11; H, 6.97. Found: C, 65.29; H, 6.97.

Reaction of $(HBzMeSi)_2O$ with $L_2(CO)ClIr$. A slurry of 538 mg (0.69 mmol) of Vaska's complex in 20 mL of benzene was heated to 55 °C. $(HBzMeSi)_2O$ (860 mg, 3.0 mmol) was then injected into the reaction flask, and the yellow solution was stirred for 30 min. At the end of this time the solution was pale yellow. The solvent was removed under reduced pressure to give an oil that was crystallized to a white solid upon trituration with petroleum ether (bp 30–60 °C). The solid was repeatedly washed with petroleum ether to remove unreacted disiloxane. The product was obtained in 80% yield: mp 170 °C dec; IR (Nujol) ν_{CO} 1960 (s), ν_{IrH} 2100 (m), SiMe 1250, 810, ν_{SiOSi} 1080, 1020 (w) cm^{-1}; ^{1}H NMR (360 MHz in C_6D_6) δ −8.04 (t, $J(^{31}PIrH)$ = 16.35 Hz, IrH, 1 H), 0.37 (s, CH_3, 6 H), δ_A 1.91, δ_B 1.79 (AB quartet, CH_2, J_{AB} = 13.37 Hz, 4 H), 7.8–6.8 (m, C_6H_5). A second triplet in the Ir–H region at δ −7.73 indicates the presence of a second isomer at about one-fifthteenth the concentration of the first isomer. However it was not possible to make definite assignments of the CH_3 and CH_2 peaks of the second isomer due to the presence of some decomposed material and its low concentration. Anal. Calcd for $C_{53}H_{51}IrO_2P_2Si_2$: C, 61.84; H, 4.96. Found: C, 61.59; H, 4.89.

Reaction of $(HPhMeSi)_2O$ with $L_2(CO)ClIr$. A slurry of 538 mg (0.69 mmol) of $L_2(CO)ClIr$ in 20 mL of benzene was heated to 55 °C. $(HPhMeSi)_2O$ (774 mg, 3.0 mmol) was then injected into the reaction flask, and the yellow solution was stirred for 30 min. The solvent was removed under reduced pressure to give an oil that solidified to a white powder when washed with petroleum ether (bp 30–60 °C). Attempts to recrystallize the product from benzene/petroleum ether resulted in some decomposition: yield 87%; mp 165–170 °C; IR (Nujol) ν_{CO} 1960 (s), ν_{IrH} 2100 (m), SiMe, 1250, 810, ν_{SiOSi} 1080 (m), 1060 (w) cm^{-1}; ^{1}H NMR (360 MHz, C_6D_6) IrH δ −7.15, −7.55, −7.68 (t, $J(^{31}PIrH)$ = 16.4 Hz), CH_3 δ 0.61, 0.70 (d, J_{PH} = 2 Hz), 0.91, 1.05 (d, J_{PH} = 2 Hz), Ph δ 7.8–6.8 (m) (integration ratio, H:Me:Ph, 1:6:40). Anal. Calcd for $C_{51}H_{47}IrO_2P_2Si_2$: C, 61.11; H, 4.69. Found: C, 60.77; H, 4.93.

Other Attempted Preparations of Metallacycles. In a screening procedure, tetramethyldisiloxane (E′E′) was used to examine the feasibility of forming various cyclometalladisiloxanes. After 20 h at 60 °C, Cp_2WH_2 showed no reaction with E′E′. $CpCo(CO)_2$ also failed to react with E′E′ after 16 h of photolysis at room temperature (some decomposition to an unidentified orange-brown, insoluble substance occurred) or after refluxing for 2 days in benzene. $CpCoLMe_2$ showed no reaction with E′E′ after 4 h at 60 °C. $L_2Ni(C_2H_4)$ reacted with E′E′ at 60 °C to give brown-black, insoluble residues, but no reaction occurred at room temperature.

Preparation of *cis*-[*trans*-1,3-Diphenyl-1,3-dimethyldisiloxanediyl]bis(triphenylphosphine)platinum(II), $L_2Pt(Ph_2Me_2Si_2O)$ (6). To a solution of $L_2Pt(C_2H_4)$ (277 mg, 0.371 mmol) in benzene (20 mL) was added via syringe 1,3-dimethyl-1,3-diphenyldisiloxane (192 mg, 0.742 mmol). The solution was stirred at 60 °C for 2 h. The red-brown solution was concentrated under reduced pressure, and a yellow-brown solid precipitated and was washed with petroleum ether (15 mL, 30/60). Recrystallization from benzene/petroleum ether gave a cream solid (mp 214–216 °C dec) in 80% yield, based on $L_2Pt(C_2H_4)$.

The infrared spectrum (Nujol) contained prominent bands at 3060 (w), 3040 (w), 1308 (w), 1240 (m), 1180 (w), 1090 (s), 1020 (w), 990 (w), 830 (s), 795 (s), 780 (s), 740 (s), 730 (s), 725 (s), 685 (s), and 660 cm^{-1}. The NMR spectrum (360 MHz) in C_6D_6 contained a broad pseudotriplet at δ −0.37 (6 H, $J(^{195}Pt)$ = 20 Hz) in addition to the phenyl multiplet at δ 6.9–7.3. Anal. Calcd for $C_{50}H_{46}P_2Si_2OPt$: C, 61.50; H, 5.72; P, 6.35; Si, 5.76; Pt, 19.99. Found: C, 60.94; H, 5.50; P, 6.55; Si, 4.70; Pt, 18.63.

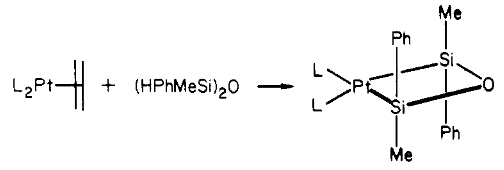
Preparation of *cis*-[1,3-Dibenzyl-1,3-dimethyldisiloxanediyl]bis(triphenylphosphine)platinum(II), $L_2Pt[(PhCH_2)_2(Me)_2Si_2O]$ (7). To a solution of $L_2Pt(C_2H_4)$[5] (676 mg, 0.905 mmol) in benzene (10 mL) was added via syringe 1,3-dibenzyl-1,3-dimethyldisiloxane (518 mg, 1.81 mmol). The solution was stirred for 2 h at 60 °C. The light yellow solution darkened to red-brown as the reaction proceeded. The benzene was removed under reduced pressure and the yellow-brown solid washed with petroleum ether (10 mL). The product was crystallized from benzene/petroleum ether at 0 °C. A cream solid (mp 180–185 °C dec) was obtained in 80% yield, based on $L_2Pt(C_2H_4)$.

The infrared spectrum (KBr disk) contained prominent bands at 3050 (w), 3020 (w), 1600 (w), 1590 (w), 1495 (m), 1380 (s), 1310 (2), 1235 (m), 1205 (m), 1200 (m), 1145 (s), 1090 (s), 1050 (m), 1020 (m), 990 (m), 890 (m), 845 (s), 800 (s), 780 (s), 750 (s), 740 (s), 730 (s), 680 (s), and 510 (m) cm^{-1}. The NMR spectrum (360 MHz) in C_6D_6 consisted of two overlapping pseudotriplets at δ −0.054 and −0.056 (6 H, $J^{195}Pt$ = 20 Hz) for the CH_3 protons and a broad set of unresolved peaks at δ 1.88–2.19 for the methylene protons (4 H) (two overlapping AB quartets further split by $J(^{195}Pt)$ and a complex set of peaks at δ 6.9–7.4 for the phenyl protons. Anal. Calcd for $C_{52}H_{50}P_2Si_2OPt$: C, 62.19; H, 5.03; P, 6.17; Si, 5.59; Pt, 19.43. Found: C, 61.55; H, 5.20; P, 6.45; Si, 5.10; Pt, 18.75.

Redistribution Reactions. Only a typical procedure will be described in detail. The exact conditions for each run will be given in the footnotes in the appropriate table. The redistribution of $(HPhMeSi)_2O$ by 6 was studied as follows: 5.0 mL (4.99 g, 19.3 mmol) of the disiloxane was added to 10 mL of a benzene solution of 6 (103 mg, 0.11 mmol) under N_2. The semimicro flask was fitted with a 20-cm reflux condenser and side arm for the inert atmosphere. During the reaction, a static blanket of N_2 was maintained in the apparatus. The mixture was stirred at 60 °C for 48 h. The volatiles were removed by trap to trap distillation under reduced pressure (25 °C) and the solvent and product fractions analyzed by GC/MS.

Results and Discussion

Our initial premise that 1,3-cross-ring interactions might lead to the specific formation of one isomeric metallacycle, e.g., **5a** over **5b** was quickly borne out in the synthesis of **6** (eq 5). The starting disiloxane $E'^{P}E'^{P}$ consists of a mixture of enantiomers (*RR* and *SS*) and the meso form (*RS*). The former should react with the Pt^0 complex to give the trans structure **5a**, while the latter would give the cis **5b**. The ^{1}H NMR spectrum of **6** shows only one type of methyl group (a 1:3:1 triplet $J(^{195}Pt)$ = 20 Hz, ^{195}Pt 34% abundance), and therefore complex **6** must be either all cis or all trans. The trans structure puts the bulky phenyl groups on opposite sides of the ring and should be more stable than the cis structure. Therefore, we assign the trans structure to **6** as shown in eq 5.



(5)

6

The reaction of $L_2Pt(C_2H_4)$ with the dibenzyldimethyldisiloxane, $(HBzMeSi)_2O$, however, gives two isomers of the metallacycle in approximately equal amounts (eq 6). The ^{1}H NMR shows two overlapping 1:3:1 triplets (J = 20 Hz) due to the coupling of the methyl groups to ^{195}Pt. The methylene region of **7** occurs between δ 1.88 and δ 2.19 and consists of an unresolved set of multiplets. Even the Me peaks in the spectra of **6** and **7** are rather broad

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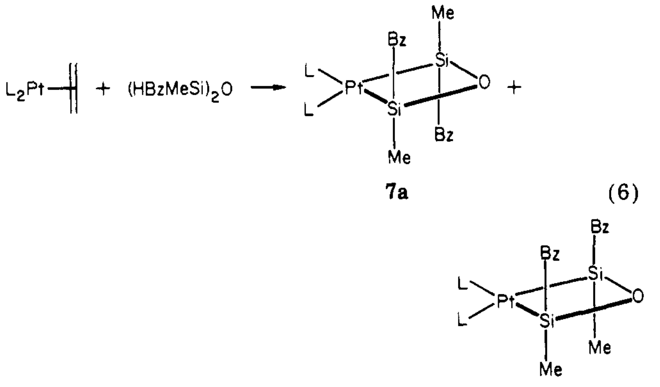
(8) Harvey, M. G.; Nebergall, J.; Prake, S. *J. Am. Chem. Soc.* **1957**, *79*, 1437.



7a (6)

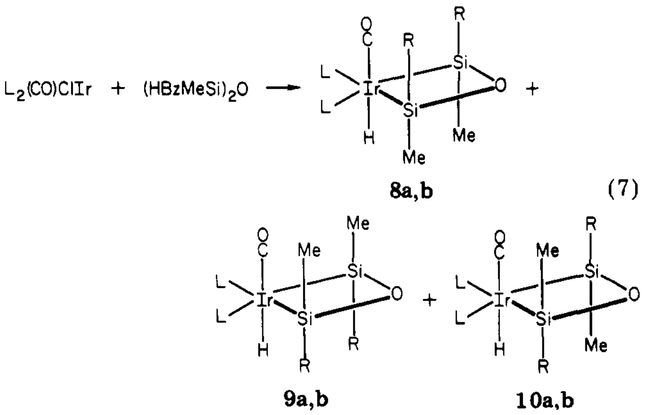
7b

presumably due to coupling with the trans and the cis phosphorus atoms. Thus, the complex nature of the methylene region of the mixture of **7a** and **7b** is readily understood, since these signals consist of two overlapping AB quartets broadened by coupling to phosphorus (the CH_2 protons are diastereotopic in both **7a** and **7b**). The centers of the two AB quartets occur at δ 1.88 and 2.10. Thus, the reaction of $L_2Pt(C_2H_4)$ with $(HPhMeSi)_2O$, but *not* $(HBzMeSi)_2O$, is stereoselective.

The conditions for the formation of the metallacycles **6** or **7** are rather critical. At room temperature, the reactions of $L_2Pt(C_2H_4)$ with the disiloxanes are too slow to be useful. At 80 °C, no metallacycles are formed. The only products were orange to red intractable solids. Similarly, if the mixtures are held at 60 °C for more than 2 h, then the orange product can form suddenly and no metallacycles can be isolated. No such problems were noted in the synthesis of the metallacycles $L_2Pt(Si_2Me_4O)$.[1b]

The IR spectra of these metallacycles are similar to those observed previously.[1b] The disiloxanes $R_3SiOSiR_3$ all have a very intense, broad absorption due to the SiO stretch in the region 1090–1030 cm^{-1}. In the metallacycles, this absorption becomes much sharper and weaker and is sometimes split into two peaks, presumably the asymmetric and symmetric stretches. In **6** and **7**, these peaks occur at 1090 (s) and 1020 (mw) cm^{-1}.

The reaction of $L_2(CO)ClIr$ with $(HRCH_3Si)_2O$ could produce a maximum of three isomers as shown in eq 7.



8a,b (7)

9a,b **10a,b**

a, R = $C_6H_5CH_2$; b, R = C_6H_5

The spectroscopic properties of the white solid isolated from the reaction of $(HBzMeSi)_2O$ with Vaska's complex are consistent with the solid being a mixture of two of the three possible isomers as shown in eq 7. Thus the IR spectrum shows two relatively weak and sharp SiO stretches at 1080 (m) and 1020 (w) cm^{-1} while the ν_{CO} and ν_{IrH} stretches occur at 1960 and 2100 cm^{-1}, respectively (cf. the corresponding values for **1c**: 1070, 1030, 1950, and 2060 cm^{-1}). The 360-MHz ^1H NMR spectrum shows (see Figure 1) two 1:2:1 triplets ($J(^{31}PIrH)$ = 16.35 Hz) at δ −7.73 and δ −8.04 in the IrH region with an integration ratio of 1:15, respectively, which indicates predominant presence of one of the two isomers. A singlet at δ 0.37 is assigned to the CH_3 resonance, while an AB quartet centered at δ 1.85 (J_{AB} = 13.37 Hz, δ_A 1.91, δ_B 1.79) is assigned to the CH_2 protons of the major isomer. It was not possible to make definite assignments for the CH_3 and CH_2 protons of the minor isomer for two reasons. First, this isomer is present in small amounts. Second, the iridium cycle undergoes slow decomposition in solution in the absence of disiloxane and the peaks arising from the decomposed material complicate the ^1H NMR spectrum.

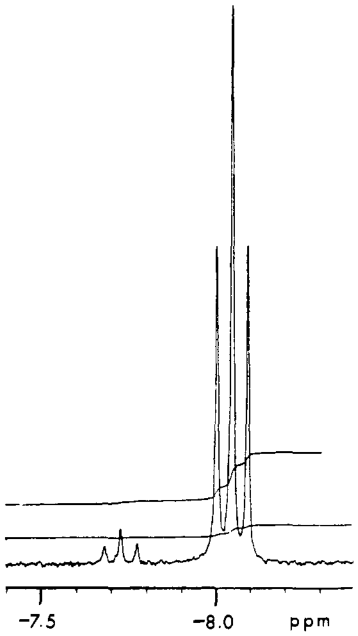


Figure 1. ^1H NMR (360-MHz) spectrum of $L_2H(CO)Ir(SiMeBzOSiMeBz)$, Ir–H region.

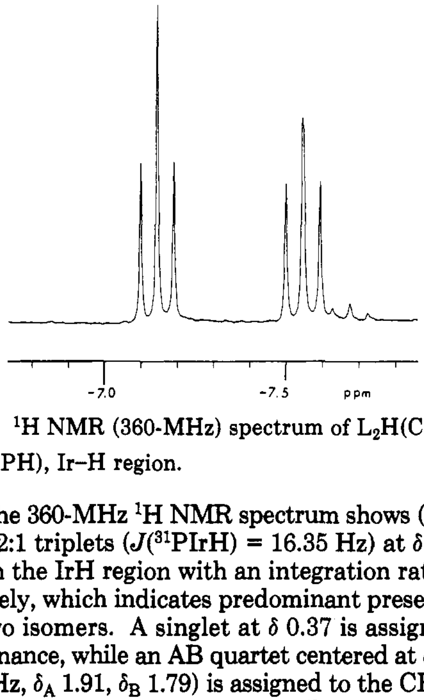


Figure 2. ^1H NMR (360-MHz) spectrum of $L_2H(CO)Ir(SiMePhOSiMePH)$, Ir–H region.

Structure **9a** has been assigned to the major isomer as *this structure provides least steric hindrance between the* Ir–CO and $Si-CH_2C_6H_5$ groups and is consistent with the single methyl resonance in the ^1H NMR. For the same reason structure **10a** is suggested for the minor isomer over structure **8a**. The product obtained from the reaction of $L_2Ir(CO)Cl$ with $(HPhMeSi)_2O$ is also a white solid. The IR and elemental analyses are fully consistent with a metallacycle with a structure similar to **1c**. The 360-MHz ^1H NMR spectrum shows (Figure 2) three triplets ($J(^{31}PIrH)$ = 1.64 Hz) in the Ir–H region at δ −7.68, −7.55, and −7.15 in an integration ratio of 1:10:9, respectively, as expected for an isomeric mixture of **8b**, **9b**, and **10b**. The methyl region consists of two broad singlets at δ 0.61 and 0.91 and two doublets (J_{PH} = 2 Hz) at δ 0.7 and 1.05. The broadening of the methyl peaks results from unresolved coupling with the trans phosphorus. The first two peaks are assigned to isomers **8b** and **9b**, and the latter two (1:1 intensities) are assigned to **10b**. The phenyl protons appear at δ 7.8–6.8 as a multiplet.

The iridium metallacycles reported in this work appear to be rather unstable in solution in the absence of disiloxanes. Thus a benzene solution of these metallacycles slowly decompose to yield a yellow, insoluble material.

The products formed from $L_2(CO)ClIr$ and the disiloxane $[H(Me_3SiO)MeSi]_2O$ also have been shown to be a mixture of three isomers corresponding to **8–10**.[9] There thus appears to be no stereoselectivity in the formation of iridium metallacycles. Platinum exhibited mixed behavior, showing selectivity for the phenylmethyldisiloxanes but not the benzylmethyldisiloxanes. Ligands with cone angles greater than that of triphenylphosphine might be more efficacious in promoting stereoselectivity in the ring-forming reactions.

The metallacycle **6** and several other metallacycle precursors were examined for their catalytic activity in causing a redistribution of groups on the disiloxanes $(HRMeSi)_2O$ (R = Ph, Bz). If these disiloxanes were to disproportionate in the same manner as tetramethyldisiloxane (eq 2),[1,9] the major products would be as shown in eq 8 and 9.

$$(n + 1)E'^PE'^P \rightarrow nPhMeSiH_2 + E'^P(D^P)_nE'^P \quad (8)$$

$$(n + 1)E'^BE'^B \rightarrow nBzMeSiH_2 + E'^B(D^B)_nE'^B \quad (9)$$

The products observed from the disproportionation of $E'^PE'^P$ catalyzed by the platinacycle **6** are shown in column 1 of Table I. Although several monosilanes, e.g., Me_3SiH, Me_2PhSiH, etc., are present, no $PhMeSiH_2$ is observed as would be expected on the basis of eq 8. However, some of the other expected products are present, e.g., $E'^PD^PE'^P$ and $E'^PD^P{}_2E'^P$ (i.e., the first two oligomers in the series). In addition to the monosilanes and expected oligomeric siloxanes, there is present a variety of other redistribution products, including disilanes and siloxanes in which methyl or hydrogen groups have been replaced by phenyl groups.

In order to better understand the products in Table I, let us first consider the metal–complex catalyzed redistribution of $PhMeSiH_2$, the silane expected to be formed according to eq 8. As Table II shows, this silane undergoes a rapid redistribution reaction under the conditions used to cause redistribution of the disiloxane $(HPhMeSi)_2O$. The products come from exchanging all the groups on the silicon for one another. For example, eq 10 and 11 detail the formation of Ph_2MeSiH and $PhMe_2SiH$ through Ph/H and Me/H exchanges, respectively.

$$MeH_2Si{-}Ph + H{-}SiHMePh \rightarrow MeSiH_3 + Ph_2MeSiH \quad (10)$$

$$PhH_2Si{-}Me + H{-}SiHMePh \rightarrow PhSiH_3 + PhMe_2SiH \quad (11)$$

These exchanges are probably close to being thermoneutral, so that the driving force is entropic, especially when a volatile; e.g., SiH_4, H_2, $MeSiH_3$, or Me_2SiH_2 may be lost. In fact, recent results suggest that the rate at which the volatiles are removed can be rate limiting and greatly effects the relative amounts of the products.[10]

Table I. Redistribution Products of 1,3-Dimethyl-1,3-diphenyldisiloxane

product	area, %		
	col 1[a,b]	col 2[c,d]	col 3[d,e]
Me_3SiH	2.1	0.4	...
$PhMeSiH_2$	...	0.2	11.3
$PhMe_2SiH$	4.8	5.9	9.1
Ph_2MeSiH	12.2	24.5	75.5
Ph_3SiH	0.7	2.7	...
Ph–Ph	0.1	6.5	2.7
$MePh_2SiSiPhMeH$	9.0	~33[f]	...
$MePh_2SiSiPhMe_2$	5.4	~0.6[g]	...
$E'E'^P$	2.9	5.1	...
$E'E^P$	...	...	1.5
E'^PE^P	10.3	3.6	...
$E'^PE'^{PP}$	6.0	0.3	
E'^PE^{PP}	1.0[h]	4.3[h]	
E^PE^{PP}	...	1.5	
$E'^PD^PE'^P$	7.2		
$E'^PD^PE^P$	1.9		
$E^PD^PE^P$	1.5		
$E'^PD^PE^{PP}$	3.5		
$E'^PD_2{}^PE'^P$	29.3		
$E'^PD_2{}^PE^P$			

[a] 0.6 mol % of **6** as catalyst in benzene at 60 °C for 48 h, 77% conversion. [b] Area % of products only, starting material and solvent removed. [c] 4.8 mol % of $Rh(acac)(C_2H_4)_2$ catalyst precursor, benzene solution, 40 °C for 1 h, ~20% conversion. [d] The GC column for these runs was not heated high enough to elute the high boiling siloxanes. [e] 0.5 M disiloxane, 1.8 mM $IrL_2(CO)Cl$ in benzene at 40 °C for 38 h, ~60% conversion. [f] Incomplete GC separation from a trace of HMePhSiOSiPhMeEt. The Et group comes from hydrosilation of the ethylene coordinated to the catalyst precursor. [g] Incomplete GC separation from a trace of $EtMePhSiOSiPhMe_2$. [h] As indicated or an isomer.

Table II. Redistribution Products of $PhMeSiH_2$

products	area, %		
	col 1[a]	col 2[b]	col 3[c]
Me_2SiH_2	3.3	...	...
$PhMeSiH_2$	10.5	...	43.3
$PhMe_2SiH$	9.8	22.5	8.4
Ph_2SiH_2	14.0	...	0.6
Ph_2MeSiH	61.0	58.6	40.1
Ph_3SiH	1.4	18.8	1.2
$(HMePhSi)_2$	...	...	6.4

[a] 5 mol % of $IrL_2(CO)Cl$ in benzene at 80 °C for 1 h. [b] 5 mol % of $IrL_2(CO)Cl$ in benzene at 80 °C for 24 h. [c] 4 mol % of RhL_3Cl in benzene at 80 °C for 30 min.

Mass balance for the products after 1 h (column 1 in Table II) shows that the ratio of groups unaccounted for is $Me_{1.1}Ph_{0.28}Si_{1.1}H_3$, which strongly suggests that the major volatile is $MeSiH_3$. After 24 h the mass balance shows that the formula for the volatiles is almost precisely $MeSiH_3$.

Column 3 of Table II shows that the rhodium-catalyzed disproportionation of $PhMeSiH_2$ is similar to the iridium-catalyzed reaction except that disilanes, e.g., $(HMePhSi{-})_2$, are formed. This result is in accord with those of Ojima et al.[11]

Silanes with only one hydrogen per silicon, e.g., $PhMe_2SiH$ (Table III), undergo metal-catalyzed redistributions much more slowly than silanes of the type R_2SiH_2. The major products again result from Ph/Me, Ph/H, and Me/H exchanges, and the mass balance indicates $MeSiH_3$ is lost as the volatile component. As in Table II, the Rh catalyst produces some disilane but the Ir catalyst does

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(9) Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *J. Organomet. Chem.* **1982**, *238*, 87.

(10) Curtis, M. D.; Proefke, M.; Gustavson, W. A., work in progress.

(11) Ojima, I.; Inaba, S.-I.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1973**, *55*, C7.

Table III. Redistribution Products of $PhMe_2SiH$

products	area, %	
	col 1[a]	col 2[b]
Me_3SiH	28.2	14.2
$PhMe_2SiH$	38.8	66.0
$PhMe_2SiCl$[c]	4.1	1.4
Ph-Ph	1.2	...
Ph_2MeSiH	16.1	13.4
Ph_2Me_2Si	8.4	2.0
Ph_3SiH	3.2	0.2
$(PhMe_2Si)_2$	...	2.9

[a] 1 mol % of $IrL_2(CO)Cl$ in benzene at 70 °C for 7 days, ~25% conversion. [b] 1 mol % of RhL_3Cl in benzene at 70 °C for 7 days, ~50% conversion. [c] Chloride from exchange with catalyst precursor.

Table IV. Redistribution Products of 1,3-Dimethyl-1,3-dibenzyldisiloxane[a, b]

product	area, %	product	area, %
$BzMeSiH_2$	2.5	Bz-Bz	7.3
$BzMe_2SiH$	36.0	$E'E'^B$	5.5
Bz_2MeSiH	30.0	$HBzMeSiSiBzH_2$	3.7
Bz_2SiH_2	3.7	HBzMeSiSiBzMeH	11.4

[a] 0.5 M disiloxane, 1.6 mM $IrL_2(CO)Cl$ in benzene at 40 °C for 45 h, 70% conversion. [b] Higher boiling siloxane oligomers not identified.

not. Since the silanes R_2SiH_2 redistribute much faster than R_3SiH, it is not unreasonable to assume that monoalkyl- or monoarylsilanes, e.g., $PhSiH_3$, would react even faster than R_2SiH_2. Therefore, the nonvolatile silanes, e.g., $PhSiH_3$, which are the expected companions of some observed products (cf. eq 11), likely undergo further, rapid redistributions and are not detected in the reaction mixtures. In other words, the concentrations of these intermediate silanes are never high enough to detect under our conditions.

Returning to the products in Table I, we now recognize the silanes and disilanes as the redistribution products of $PhMeSiH_2$, formed by the disproportionation shown in eq 8. The "expected" oligomeric siloxanes $E'^PD^P{}_nE'^P$ are formed as a result of SiO/H exchange as shown in eq 12.

$$\begin{gathered}\text{HPhMeSi–OSiMePhH} + \text{H–SiMePhOSiMePhH} \rightarrow \\ \text{PhMeSiH}_2 + \underset{E'^PD^PE'^P}{\text{HPhMeSiO–SiMePh–OSiMePhH}} \quad (12)\end{gathered}$$

The remaining disiloxanes, e.g., E'^PE^P (= $HPhMeSiOSiMe_2Ph$), are the result of Me/H, Ph/Me, and Ph/H exchanges on the starting disiloxanes or on the oligomeric siloxane products.

The disproportionation of $E'^BE'^B$ was not studied extensively, but the data in Table IV show that this reaction follows a course parallel to that of the disproportioantion of $E'^PE'^P$. The lower boiling products are all scrambling products of the $BzMeSiH_2$ formed in the initial reaction (cf. eq 9).

The observation of these rather extensive rearrangements that occur under relatively mild conditions naturally raises the question of the mechanism. Recent work on the redistribution of tetramethyldisiloxane[9,12] suggests that, although metallacycles are formed ubiquitously in the reaction of low-valent Ir, Rh, or Pt complexes with $(HR_2Si)_2O$, these metallacycles probably are not directly involved in the catalytic cycles that lead to redistribution. The very rapid redistribution of $PhMeSiH_2$ also shows that metallacycles e.g. 1, are not required to produce the observed effects.

An extensive discussion of mechanistic possibilities is presented in ref 1c and will not be repeated here. It is clear, however, that the low-valent species easily insert into Si–C bonds, as well as into Si–H bonds. The observed coupling products, e.g., biphenyl or bibenzyl (Tables I, III, IV) show that either multiple insertions occur on one center or some reductive eliminations are binuclear.[13] Silylene-bridged, dinuclear species have been suggested as possible intermediates.[1c]

Summary

The initial impetus behind this work was a desire to catalytically disproportionate the disiloxanes $(HRMeSi)_2O$ into $RMeSiH_2$ and stereoregular siloxanes $E'^RD^R{}_nE'^R$. Formation of one metallacycle, viz. **6**, is stereoselective. However, the catalyzed disproportionation of the disiloxanes is much more complex than originally conceived and it is unlikely that this route will be useful for the synthesis of stereoregular silicones.

However, these redistribution reactions point up our need for a more detailed understanding of "decomposition" processes for silyl transition-metal complexes and for the synthesis of a wider range of model silyl complexes.

Acknowledgment. We thank the Office of Naval Research for support of this research. A loan of precious metals from the Johnson Matthey, Inc., is gratefully acknowledged. The GC/MS system was purchased with the aid of NSF Grant No. CHE77-11338.

Registry No. **4** (R = Bz), 85028-96-2; **4** (R = Ph), 6689-22-1; **6**, 85028-94-0; **7a**, 85028-95-1; **7b**, 85081-46-5; **8b**, 85028-93-9; **9a**, 85028-92-8; **9b**, 85081-45-4; **10a**, 85081-43-2; **10b**, 85081-44-3; Bz_2MeSiH, 1631-71-6; BzMeSiHCl, 18246-08-7; PhMeSiHCl, 1631-82-9; $PhMeSiH_2$, 766-08-5; $PhMe_2SiH$, 766-77-8; $(Ph_3P)_2(CO)ClIr$, 14871-41-1; $(Ph_3P)_2Pt(C_2H_4)$, 12120-15-9.

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[12] Gustavson, W. A.; Curtis, M. D., manuscript in preparation.

[13] Binuclear reductive elimination pathways have been documented, see: Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.