Table I. 1D ^{13}C and ^{1}H NMR Spectra of Purified Regioisomers of $C_{60}[OsO_4(4\text{-}tert\text{-butylpyridine})_2]_2$

isomer	^{13}C peaks for C_{60} moiety[a]	C–O peaks	4-*tert*-butylpyridine signals[b]	symmetry	possible structures[c]
2	30 (equal intensity)	2	2	C_2	c, g (f)
3	30 (equal intensity)	2	2	C_2	f (c, g)
4	32 (4 half intensity)	2	2	C_s	a, b, e, w, x
5	32 (4 half intensity)	3 (ratio 1:1:2)	3 (ratio 1:1:2)[d]	C_s	d (y, z)

[a] See supplementary material for a complete peak listing. [b] All ^{13}C and ^{1}H NMR peaks resolve except as noted for isomer **5**. [c] Assignments in parentheses are consistent with 1D spectra but ruled out by 2D spectra. [d] C(2)-*H* shows two peaks (ratio 3:1) and the *tert*-butyl signals overlap.

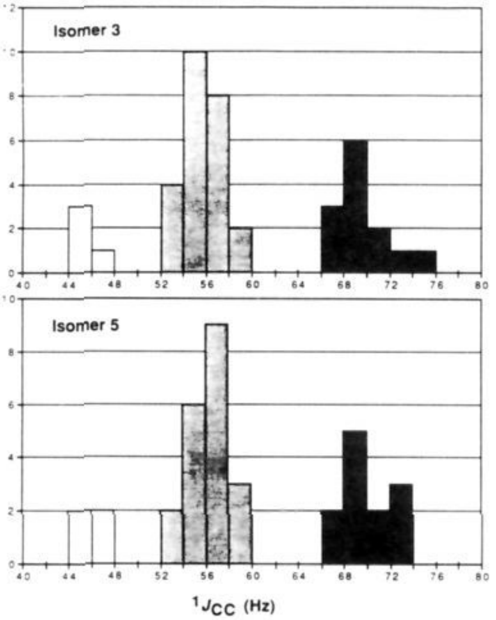
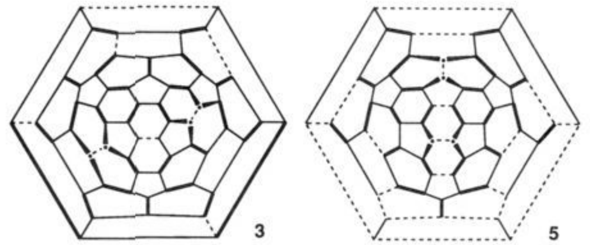


Figure 2. Histograms of coupling constants ($^1J_{CC}$) in isomers **3** and **5** showing distinction of C–C–O bonds (white), 6,5 ring fusions (shaded), and 6,6 ring fusions (black).



3 5

Figure 3. Pattern of coupling constants in isomers **3** and **5**: 45–47 Hz (wedges), 53–59 Hz (solid lines); 67–74 Hz (bold lines). Dots indicate O-bonded carbons; dashed lines indicate undiscernible couplings.

in monoosmylated C_{60},[4] we used the more powerful C–C HOHAHA technique[9] to assign the 30 and 32 types of carbons in bisosmylated isomers **3** and **5**.[10] The O-bonded carbons are the furthest upfield (103–105 ppm), the adjacent carbons tend to be downfield (149–157 ppm), and the remaining carbons are dispersed between 136 and 151 ppm (see supplementary material for complete assignments). Long-range couplings aided peak assignments. With isomers **3** and **5** identified, isomers **1**, **2**, and **4** can be tentatively assigned as shown in Figure 1 on the basis of the symmetries of isomers **2** (C_2) and **4** (C_S) and the elution order on HPLC (assuming that polarity increases as the angle between the osmyl groups decreases). These assignments agree with the steric and electronic control proposed above to account for the formation of five regioisomers of $C_{60}[OsO_4(py)_2]_2$, i.e., steric blocking of the hemisphere proximate to the first osmyl group and addition of the second osmyl group to a 6,6 ring fusion.

Coupling constants ($^1J_{CC}$) for isomers **3** and **5** indicate three types of bonds within the C_{60} clusters: bonds to the O-bonded carbons (45–47 Hz), 6,5 ring fusions (53–59 Hz), and 6,6 ring fusions (67–74 Hz) (Figure 2). Thus, these difunctionalized C_{60} derivatives with differently contoured band-shaped π-systems exhibit confined local distortion at the sites of osmylation, with the remainder of the carbon framework showing bond alternation corresponding to the two types of bonds in C_{60} (Figure 3).

Acknowledgment. J.M.H. is grateful to the National Science Foundation (Presidential Young Investigator Award, CHE-8857453), the Camille and Henry Dreyfus Foundation (Teacher–Scholar Award), the Merck Sharp & Dohme Research Laboratories (postdoctoral fellowship for A.M.), the Shell Oil Company Foundation (Shell Faculty Fellowship), Xerox Corporation, Monsanto Company, Hoffmann-La Roche Inc., and Eli Lilly and Company for financial support. U.B. thanks the Deutsche Forschungsgemeinschaft for a postdoctoral fellowship. We thank Alessandro F. Moretto for assistance with the synthesis of ^{13}C-enriched C_{60} and Virginia A. Carlson for assistance in baking the packed carbon rods.

Note Added in Proof: 2D NMR analysis of isomer **2** confirms the assignment given in Figure 1.

Supplementary Material Available: Listing of ^{13}C and ^{1}H NMR peaks for isomers **2–5** including peak assignments for isomers **3** and **5** (2 pages). Ordering information is given on any current masthead page.

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[9] Nunlist, R.; Ball, G. E.; Meyer, A.; Hawkins, J. M. Manuscript in preparation.

[10] 2D spectra were obtained of **3** (44 mg) and **5** (35 mg) in $CDCl_3$ at 100.627 MHz on a modified Bruker AM-400 using a 5-mm probe at 26 °C. A HOHAHA[11] sequence with 10 ms MLEV-17 mixing time was used. The spectral width was set to 7042 Hz in both dimensions; 4K or 8K points were sampled in F_2 and 1024 to 2048 points were sampled in F_1. The files were processed on a Bruker X32. After application of an exponential broadening of 4 Hz in F_2 and squared cosine multiplication in F_1, 4K points in F_2 and 1K points in F_1 were transformed with zero-filling to a final 4K × 4K complex matrix. Coupling constants were measured from individual rows.

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Reaction of Disilanes with a *cis*-Platinum Dihydride: Novel Platinum Complexes with Terminal Disilanyl Groups and Bridging Disilene Ligands

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Received March 16, 1992

Catalytic dehydrogenative coupling of polyhydrosilanes to polysilane oligomers and polymers has been a growing area of interest.[1,2] Recent work has focused on early transition metal

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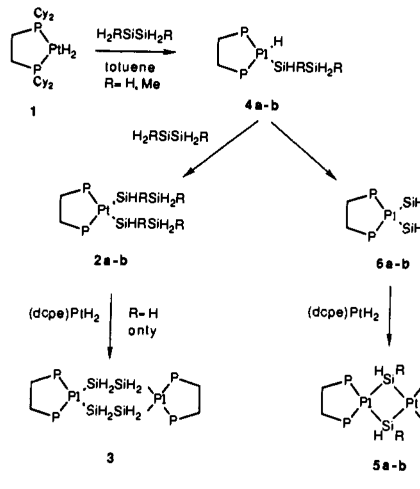
Scheme I



catalysts which are proposed to polymerize silanes via a σ-bond metathesis mechanism.[2] However, oxidative addition–reductive elimination steps may be more important for the late metals such as platinum.[2c,3] In the course of examining platinum-mediated dehydrogenative coupling of silanes, we have investigated the reactions of disilane (H_3SiSiH_3) and 1,2-dimethyldisilane ($MeSiH_2SiH_2Me$) with *cis*-(dcpe)PtH_2 (**1**) (dcpe = 1,2-bis(dicyclohexylphosphino)ethane).[4] We now report the synthesis of the first isolated example of a platinum complex containing terminal disilanyl (Si_2H_5) groups[5] as well as an unusual Pt_2Si_4 ring system containing bridging disilene (Si_2H_4) units.[6]

Rapid addition of H_3SiSiH_3 to toluene solutions of **1** between 25 and 40 °C results in an immediate yellow color which disappears after 10–15 s, producing only (dcpe)$Pt(SiH_2SiH_3)_2$ (**2a**) and $[(dcpe)Pt]_2(\mu\text{-}SiH_2SiH_2)_2$ (**3**) in a 4:1 ratio.[7] A slower rate of disilane addition increases the amount of ring compound **3** such that a near 1:1 ratio of **2a** to **3** is obtained. Complexes **2a** and **3** arise from simple oxidative addition–reductive elimination steps involving the initial formation of the disilanylplatinum hydride **4a**, which further reacts with disilane giving **2a** (Scheme I). In the presence of excess **1**, complex **2a** undergoes a ring-closing oxidative addition–reductive elimination sequence to give **3**. Independent reaction of **1** with **2a** at room temperature produces **3** quantitatively.

The new complexes **2a** and **3** have been isolated as white crystalline solids.[8] The bis(silyl) complex **2a** is air-sensitive, whereas the unusual ring compound **3** is stable to air both as a solid and in solution. An X-ray structure of the toluene solvate **3·4PhCH$_3$** is shown in Figure 1. The central ring of complex **3** adopts a chair conformation and represents the first example of a Pt_2Si_4 ring core.

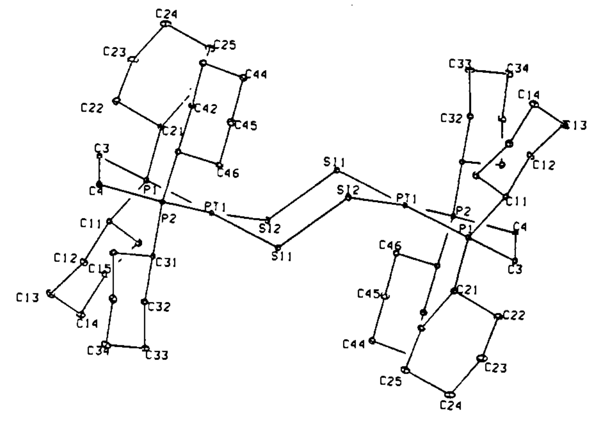


Figure 1. Molecular structure of **3** showing Pt_2Si_4 ring core. Hydrogen atoms have been omitted for clarity. Significant bond lengths (Å) and angles (deg): Pt(1)–Si(1), 2.378 (1); Pt(1)–Si(2), 2.369 (1); Pt(1)–P(1), 2.301 (1); Pt(1)–P(2), 2.293 (1); Si(1)–Si(2), 2.355 (2); Si(1)–Pt(1)–Si(2), 83.13 (5); Pt(1)–Si(1)–Si(2), 116.97 (7); P(1)–Pt(1)–P(2), 87.13 (5).

Much slower additions of H_3SiSiH_3 to **1** in toluene produce yellow solutions whose colors do not dissipate with time. NMR analysis reveals, along with **3** (28%), the formation of a new orange compound $[(dcpe)Pt]_2(\mu\text{-}SiH_2)_2$ (**5a**) in 51% yield. Similar ring systems have resulted from the reaction of monosilanes with low-valent platinum species;[9] however, this is the first example of such a ring with only hydrogens on silicon.

We believe that **5a** arises from reaction of the bis(silyl) complex **6a** with **1** in a manner parallel to the formation of **3** from **2a** and **1**. Supporting evidence is provided by reaction of the closely related disilane, $MeSiH_2SiH_2Me$, with **1**. Rapid addition of 1 equiv of $MeSiH_2SiH_2Me$ to **1** in toluene at 25 °C gives a quantitative yield of the bis(silyl) complex **6b**.[10] In contrast, slower addition at 40 °C gives exclusively the two geometric isomers of $[(dcpe)Pt]_2(\mu\text{-}SiHMe)_2$ (**5b**). Independent reaction of **6b** with **1** at 40 °C affords **5b** quantitatively; similarly, **6a** is found to react with **1** at room temperature to give **5a**.[11]

The formation of the bis(silyl)s **6a,b** is unexpected and involves the cleavage of an Si–Si bond from the unstable disilanylplatinum hydrides **4a,b**. The reaction of 1 equiv of $MeSiH_2SiH_2Me$ with **1** in toluene-d_8 was monitored by NMR. Addition of $MeSiH_2SiH_2Me$ to **1** at −80 °C results in rapid oxidative addition to give the Pt(IV) intermediate, *fac*-(dcpe)$Pt(SiMeHSiMeH_2)H_3$. Upon warming to −25 °C, this octahedral complex loses hydrogen, producing the disilanylplatinum hydride **4b**. Further warming to room temperature results in the disappearance of **4b** with concomitant formation of the bis(silyl) **6b**.

The transformation of disilanylplatinum hydrides to bis(silyl)platinum complexes represents a key step in the platinum-catalyzed redistribution reactions of 1,2-dihydrodisilanes. Yamamoto proposed that these reactions proceed via an α-silyl shift

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[6] An unusual complex containing a μ-$^1\eta$,$^1\eta$-PhHSiSiHPh ligand bridging Pt(IV) centers has been recently characterized: Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 1917–1919.

[7] **Caution!** Disilane is a pyrophoric gas which forms explosive mixtures with air. Proper precautions should be observed in the handling of this material.

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[10] Bis(silyl) platinum complexes have also been observed from the reaction of $PhSiH_2SiH_2Ph$ with $Pt(PEt_3)_3$; see ref 6.

[11] The formation of Pt_2Si_2 rings from the reaction of 1,2-diphenyldisilane with $(Et_3P)_2PtCl_2$ and Na has been recently reported (ref 9d). An η^2-disilene platinum complex was proposed as an intermediate.

to give a Pt(IV) silyl–silylene intermediate.[12] Similar α-silyl shifts have been proposed by Pannell and by Ogino in photochemical reactions of polysilyl iron complexes.[13] However, an alternative route is via η^2-disilene intermediates, followed by fast back-reaction with dihydrogen. Stable platinum η^2-disilene complexes have been reported by Pham and West to undergo facile hydrogenolysis of the silicon–silicon bond to yield platinum bis(silyl)s.[14] Investigations into the nature of this process are currently in progress.

Acknowledgment. M.J.F. thanks the Tulane Center for Bioenvironmental Research and the Tulane Committee on Research for support of this work. We also thank Drs. Fred Davidson and Joseph Lazar (Du Pont) and Drs. Brian Tobias and Deborah A. Grimm (Tulane University Coordinated Instrumentation Facility) for assistance with NMR and mass spectra. The expert technical assistance of Chris Adams, Will Marshall, and John Nguyen is greatly appreciated.

Supplementary Material Available: Listings of NMR, MS, and elemental analysis data, tables of crystal data, atomic coordinates and temperature factors, hydrogen coordinates, and intramolecular bond distances and angles (12 pages); tables of calculated and observed structure factors of **3** (19 pages). Ordering information is given on any current masthead page.

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Selective-Solvation-Induced Intramolecular Electron Transfer: Time Resolution via Pulsed Accelerated Flow Spectrophotometry

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Received November 25, 1991
Revised Manuscript Received August 3, 1992

Despite extensive theoretical interest, relatively few experimental reports exist concerning *nonphotochemical* intramolecular electron-transfer (ET) kinetics, at least for chemically reversible (i.e., thermodynamically well-defined) redox systems.[1-3] Nevertheless, the few that do exist[1,2] have yielded important insights concerning donor–acceptor electronic coupling and solvent reorganization, especially over longer distances. We wish to report here an experiment which adds in an unusual way to the limited list of both chemical systems and chemical methodologies for inducing intramolecular ET.[4] Our approach is based on the ability of added solvent to influence redox potentials, and therefore oxidation-state distributions, in selected asymmetric mixed-valence systems.[5,6]

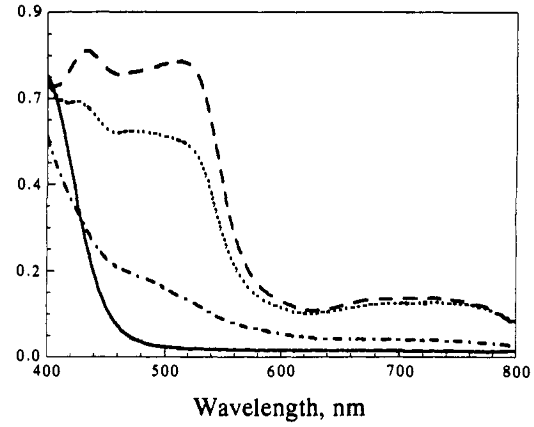
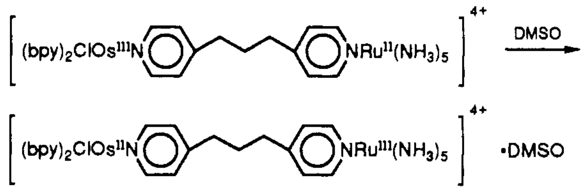


Figure 1. Visible absorption spectra for the following: $(NH_3)_5Ru^{II}$(4-methylpyridine)$^{2+}$ in NM (—); $(bpy)_2ClOs^{III}(TMB)Ru^{II}(NH_3)_5{}^{4+}$ in NM (-··-); $(bpy)_2ClOs^{II}(TMB)Ru^{III}(NH_3)_5{}^{4+}$ in 88% NM, 8% CH_3CN, and 4% DMSO (···); $(bpy)_2ClOs^{II}$(4-methylpyridine)$^+$ in 88% NM, 8% CH_3CN, and 4% DMSO (- - -). (Residual Os^{II} absorption for the nominal $Os^{III}(TMB)Ru^{II}$ probably orginates from slight redox isomerization.)

The system we have examined is a trimethylenebipyridine-bridged ruthenium/osmium complex (**1**) in nitromethane (NM) as the parent solvent:[7]



(1)

As shown by Figure 1, addition of as little as 4 vol % dimethyl sulfoxide (DMSO) is sufficient to convert the visible absorption spectrum from one largely characteristic of $(NH_3)_5Ru^{II}$(pyridine-CH_3) to one indicative of the presence of a $(bpy)_2ClOs^{II}$(pyridine-CH_3) fragment.[5a] (Note that the metal(III) fragments are nearly transparent in the green and red portions of the spectrum.) Quantitative spectral experiments show that, when 4% DMSO is present, redox trapping at Os is favored by 16-fold ($\Delta G_{Et} = -1.6$ kcal mol^{-1}) over trapping at Ru. From previous studies[5,6] the redox isomerization is known to arise from negative shifts in the Ru–ammine formal potential. The shifts are associated with preferential solvation and stabilization of the Ru(III) oxidation state via specific ammine/solvent interactions.

To time resolve the electron transfer we have employed a rapid (microsecond) mixing technique: pulsed accelerated flow (PAF) spectrophotometry. PAF is a highly efficient (in terms of time and reagent consumption) multiple-velocity variant of continuous flow spectrophotometry and has been described in detail by Margerum and co-workers.[8] In our experiments a solution of **1** in 100% NM was rapidly mixed with a solution containing 72% NM, 20% CH_3CN, and 8% DMSO. (Acetonitrile was required in order to achieve refractive index matching and eliminate Schlieren scattering effects[7] which can accompany mixing.) The

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