Figure 1. Crystal and molecular structure of Sc(OEP)(η^5-C$_5$H$_5$). Thermal ellipsoids are depicted at the 75% probability level. Selected distances (Å): Sc–N(av) 2.190 (3), Sc–C(Cp)(av) 2.494 (4), Sc–Cp centroid 2.196. Selected bond angles (deg): Cp–Sc–N(av) 111.28, N(1)–Sc–N(2) 82.1 (1), N(1)–Sc–N(4) 82.7 (1), N(2)–Sc–N(3) 82.4 (1), N(3)–Sc–N(4) 82.4 (1).

Compounds **2a–c** are air-stable, sublimable solids that can be dissolved in a variety of aerated polar and nonpolar solvents without decomposition. In the EI mass spectrum, intense peaks were observed for the molecular ions (OEP)Sc(η^5-Cp)$^+$ (*m/e* 642, 57% in **2a**, 712, 37% in **2b**) and signals due to (OEP)Sc$^+$ (100%) formed by loss of the Cp ligand. As expected, the OEP ethyl groups are diastereotopic showing complex multiplets for the methylene hydrogens by ^{1}H NMR spectroscopy. More surprising are the pronounced upfield shifts in ^{1}H NMR signals of the cyclopentadienyl substituents resulting from strong ring currents in the porphyrin core. In **2a** for example, the η^5-C$_5$H$_5$ protons resonate at δ 1.68, far outside the usual range of δ 4–6. Methyl substituents on cyclopentadienyls experience shielding of a similar magnitude; for instance, the Cp* methyls in **2b** are seen at δ –0.61. The latter value is similar to that observed by Sewchok et al. during their attempted preparation of (TTP)ScCp* (δ –0.42), a tetraarylporphyrin analogue to **2a–c**; this material was reportedly hydrolytically sensitive and could not be isolated.[3] UV–vis spectra of **2a–c** closely resemble the starting chloride **1**.

The unusual nature of these compounds called for complete structural characterization by X-ray crystallography; the results for the Cp derivative **2a** are displayed in Figure 1.[10] The scandium is regularly coordinated by the four porphyrin nitrogens and the η^5-Cp ligand; bond distances to the individual atoms in each ligand are identical within experimental error with Sc–N(av) = 2.190 (3) Å and Sc–C(av) = 2.494 (4) Å. In the related derivatives (TTP)ScCl[3] and Cp*$_2$ScMe,[11] the corresponding values are Sc–N(av) = 2.17 (3) Å and Sc–C(av) = 2.46 (1) Å, respectively. In **2a** the scandium is 0.80 Å from the mean plane of the nitrogens and 2.196 Å from that of the Cp; the latter is planar to within less than 1 esd. The porphyrin core is only slightly ruffled, with rings 1 and 3 tilted "down" from the scandium and rings 2 and 4 twisted "up"; angles between the pyrrole planes and the mean plane of the porphyrin are –1.7°, 5.6°, –1.7°, and 5.6° for pyrroles 1–4, respectively. Parameters associated with the Cp ligand are unexceptional, and there are no particularly close interactions between adjacent molecules.

(10) Crystal data for **2a**: ScN$_4$C$_{41}$H$_{49}$; space group *P*2$_{1/c}$ with *a* = 13.534 (4) Å, *b* = 17.326 (5) Å, *c* = 15.296 (5) Å, β = 102.89 (2)°, *V* = 3497 (4) Å^3, d_{calcd} = 1.22 g cm^{-3}, and *Z* = 4. Data collected on an Enraf-Nonius CAD-4 diffractometer at –115 °C with Mo Kα (λ = 0.71073 Å). A 2θ range from 3° to 45° gave 4558 unique data. The structure was solved by direct methods (MULTAN) and refined by least-squares and Fourier techniques using 415 variables against 3062 data for which $F^2 > 3\sigma(F^2)$, to give *R* = 5.20%, R_w = 6.42%, and GOF = 1.68. For all 4558 data *R* = 8.50%. The crystal structure was determined by Dr. F. J. Hollander, staff crystallographer at the U. C. Berkeley Crystallographic Facility (CHEXRAY).

(11) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

Synthesis and Reactivity of Cp$_2$Ta(CH$_2$)$_2$Ir(CO)$_2$: An Early–Late Heterobimetallic Complex That Catalytically Hydrogenates, Isomerizes, and Hydrosilates Alkenes

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Despite the plethora of soluble early–late heterobimetallic complexes that have been prepared,[1] few are known that exhibit catalytic activity as intact binuclear species.[2] As an extension of our earlier studies of tantalum–platinum and –cobalt complexes,[3] we have carried out the synthesis and chemistry of the new complex Cp$_2$Ta(μ-CH$_2$)$_2$Ir(CO)$_2$ (**1a**). We report here our preliminary finding that complex **1a**, which is surprisingly air and water stable, catalytically hydrogenates, isomerizes, and hydrosilates olefins under mild conditions. We have also obtained direct NMR evidence under catalytic operating conditions that **1a** remains intact during the reaction. Despite the similarity of the hydrogenation and hydrosilation processes, a kinetic study of the reactions of **1a** shows that they proceed by different mechanisms.

As illustrated in Scheme I, treatment of Cp$_2$Ta(CH$_2$)(CH$_3$)[4] with (η^5-indenyl)Ir(CO)$_2$[5] leads to the extrusion of 1 equiv of indene and the formation of bis-bridging methylene complex **1a** in 88% isolated yield. The related complex **1b** can be prepared by using the analogous starting material Cp(η^5-C$_9$H$_7$)Ta(CH$_2$)(CH$_3$). Although we have not been able to obtain X-ray quality crystals of **1a**, it is quite similar in spectroscopic properties to **1b**, and a crystal structure of the latter complex has been completed. In this material, the tantalum center is pseudotetrahedral (like its mononuclear alkylidene precursor) and the iridium center is square planar. The Ta–CH$_2$ distance in **1b** (2.132 (8) Å) (Figure 1) is intermediate between average Ta—CH$_2$R (2.26 Å) and Ta=CHR (2.02 Å) bond lengths.[6] The Ta–Ir bond length of 2.858 (1) Å is consistent with the presence of a metal–metal single bond. We assume that the mechanism of formation of these materials is related to that proposed earlier for the formation of Cp$_2$Ta(CH$_2$)$_2$Pt(H)PMe$_3$.[3a]

In the presence of H$_2$, compound **1a** catalyzes the hydrogenation of ethylene and the isomerization of higher olefins.[7] Isomerization does not occur in the absence of H$_2$. However, chemoselectivity depends on the solvent used. Thus, in benzene at 45 °C, ethylene is the only alkene hydrogenated (1 turnover/3 h); mono- and disubstituted alkenes isomerize at a similar velocity to an equilibrium mixture of *E* and *Z* internal alkenes. In THF at 45 °C,

(1) For a review, see: Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

(2) For some recent examples, see: (a) Gelmini, L.; Stephan, D. W. *Organometallics* **1988**, *7*, 849. (b) Choukroun, R.; Dahan, F.; Gervais, D.; Rifai, C. *Organometallics* **1990**, *9*, 1982 and references cited therein.

(3) (a) Jacobsen, E. N.; Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 3706. (b) Goldberg, K. I.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4853.

(4) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(5) Foo, T. Ph.D. Dissertation, University of California, Berkeley, CA, 1989.

(6) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1986**, *303*, 39.

(7) For reviews of homogeneous hydrogenation, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapter 10. (b) James, B. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1983.

Scheme I
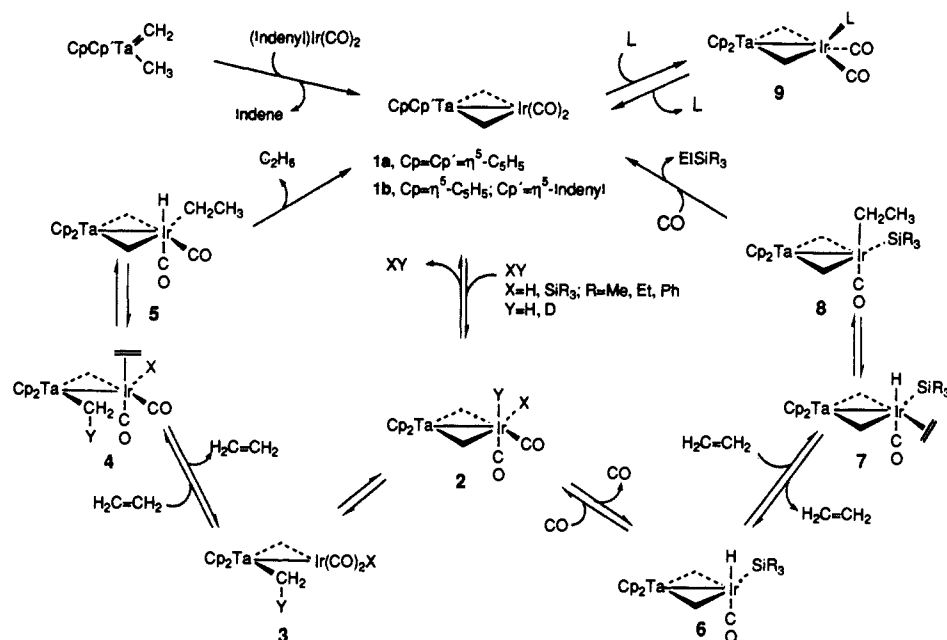
however, overall rates are higher,[8] both ethylene and 1-alkenes are hydrogenated (1 turnover/h), and disubstituted alkenes once again undergo only isomerization. Compound **1a** is the sole organometallic species detected by ^{1}H NMR spectrometry during these reactions.

Compound **1a** is also a hydrosilation catalyst.[9] A variety of silanes can be used (Me$_3$SiH, Et$_3$SiH, Ph$_3$SiH), but only ethylene is hydrosilated; higher alkenes are isomerized. In contrast to the hydrogenation results described above, changing solvent has no effect on the selectivity or rate of hydrosilation. In this case two complexes (compound **1a** and a material isolated and identified as oxidative addition product **2**, X = SiPh$_3$, Y = H) were detected by ^{1}H NMR monitoring in a ratio dependent on the concentration of **1a** and silane.

In the absence of alkene, reaction of compound **1a** with either D$_2$ or Et$_3$SiD in THF or benzene results in the incorporation of

deuterium into the μ-CH$_2$ positions with concomitant formation of HD or Et$_3$SiH. It seems likely that after H$_2$ or Et$_3$SiH undergoes oxidative addition at the iridium center, reversible reductive elimination/oxidative addition of one of the methylene bridges (as illustrated in Scheme I) is responsible for isotope exchange into the bridging positions. A similar process was identified for Cp$_2$Ta(CH$_2$)$_2$Pt(H)(PMe$_3$).[3a] However, the different response to changes in solvent exhibited by the hydrogenation and hydrosilation processes suggests that they proceed by different mechanisms.

Kinetic studies support this inference. The rates of hydrogenation and hydrosilation were obtained by monitoring the disappearance of ethylene by ^{1}H NMR spectrometry vs an internal standard (ferrocene for hydrogenation; 1,3,5-trimethoxybenzene was used in the hydrosilation) at 45 °C in benzene. Both rates were first order in catalyst and H$_2$ or silane.[10] The hydrogenation was also first order in alkene, but the rate of the hydrosilation was independent of the alkene concentration. The rate of deuterium exchange into the bridging methylene positions is at least 16 times faster than the rate of ethylene hydrogenation.[11]

On the basis of these observations, we propose the mechanisms shown in Scheme I for these catalytic reactions. After oxidative addition of XY (X = H, R$_3$Si; Y = H, D) to the iridium center, the rates of the deuterium-exchange studies require that under either hydrogenation or hydrosilation conditions species **1, 2,** and **3** are in rapid equilibrium. Alkene complex **4** is probably also formed reversibly in both systems. However, in hydrogenation, where both X and Y = H, migration of X to the coordinated alkene in **4** can take place rapidly. In contrast, migration of Y = SiR$_3$ is much slower, preventing hydrosilation from proceeding by this pathway. With hydrosilation blocked by the slow silyl migration in **4**, we suggest that it proceeds by the cycle shown
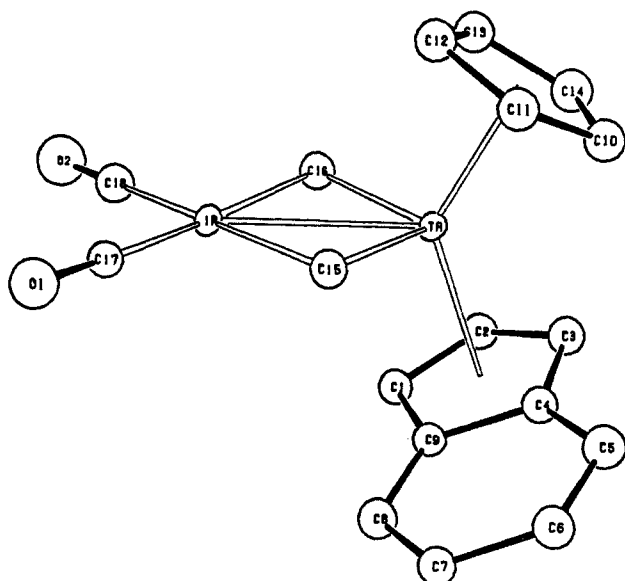

Figure 1. ORTEP diagram illustrating the structure of (indenyl)(Cp)Ta-(CH$_2$)$_2$Ir(CO)$_2$ (**1b**). Selected bond distances (Å): Ir–Ta, 2.858 (1); Ir–C15, 2.181 (8); Ir–C16, 2.167 (8); Ta–C15, 2.126 (8); Ta–C16, 2.138 (8); Ta–Cp, 2.151; Ta–indenyl, 2.098. Selected bond angles (deg): Ta–C15–Ir, 83.1; Ta–C16–Ir, 83.2; C17–Ir–C18, 97.9; Cp–Ta–Ir, 109.9; indenyl–Ta–Ir, 117.3; C15–Ir–C16, 95.4; C15–Ir–C17, 83.4.

(8) Polar solvents increase the rate at which Wilkinson's catalyst hydrogenates olefins; cf.: Hussey, A. S.; Takeuchi, Y. *J. Am. Chem. Soc.* **1969**, *91*, 672.

(9) For reviews of hydrosilation, see: (a) Ojima, I. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: New York; 1989; Chapter 25. (b) Harrod, J. F.; Chalk, A. J. In *Organic Syntheses via Metal Carbonyls*, Wender, I., Pino, P., Eds.; John Wiley and Sons: New York, 1979; Vol. 2, p 673. (c) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(10) A case has been made that hydrosilation with at least some catalyst precursors may be a heterogeneous reaction (Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998 and references cited therein). In our system we see no evidence for this; the reactions proceed smoothly, and catalyst **1** remains stable and soluble throughout the reaction.

on the right side of Scheme I. Dissociation of CO from **2** gives coordinatively unsaturated intermediate **6**. Coordination of ethylene leads to **7**, an intermediate in which H (rather than only SiR₃, as in **4**) can migrate to the alkene.[12]

In summary, Cp₂Ta(CH₂)₂Ir(CO)₂ is a unique catalytically active heterodinuclear complex. The reactions it induces appear to take place at the iridium center, but the tantalum is necessary for the chemistry observed to take place,[13] although the specific role played by the early metal remains to be elucidated. Studies are in progress aimed at obtaining further evidence for the mechanistic conclusions summarized above, understanding the solvent effect observed in the hydrogenation reaction, and modifying the structure of **1a** to increase the scope of its catalytic reactivity.

Supplementary Material Available: Complete spectroscopic and analytical data for **1a,b**, **2a–c**, and **9** and details of the crystal structure determination for **1b**, including crystal and data collection parameters, positional parameters, and tables of intramolecular distances and angles (6 pages). Ordering information is given on any current masthead page.

(11) Kinetic data were collected by monitoring the disappearance of the bridging methylenes against ferrocene as an internal standard by ¹H NMR spectrometry.

(12) We propose that the rate-determining step of the hydrosilation reaction involves reversible loss of CO from iridium. This predicts that added CO should inhibit the hydrosilation. Unfortunately, this prediction is difficult to test because added CO (as well as other dative ligands, such as PMe₃) forms stable adduct **9** with **1** and retards the rate by this mechanism (Scheme I).

(13) It is not easy to find structurally analogous mononuclear iridium complexes whose catalytic properties can be compared with those of **1**. One candidate is the phosphorus/iridium compound (Ph₂P(CH₂)₂)Ir(CO)(PPh₃), which we have recently prepared and shown to have a structure similar to **1**. This material is at least 100 times less active than **1** (or its phosphine analogue Cp₂Ta(CH₂)₂Ir(CO)(PPh₃)) in hydrogenation and hydrosilation reactions (Butts, M. D.; Bergman, R. G., unpublished results). The comparative chemistry of the tantalum and phosphorus compounds will be reported in a full paper.

Use of Alkyl Substitution To Control Ring Size in the Intramolecular Ionic Diels–Alder Reaction

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We have previously demonstrated that derivatives of the bicyclo[4.3.0]nonyl ring system could be prepared in high yield via an ionic Diels–Alder reaction from derivatives of 1,3,8,10-undecatetraene.[2] Determination of the site of protonation and the regioselectivity of the addition of the allyl cation to the 1,3-diene, through careful manipulation of the methyl substitution pattern on the tetraene,[3] has been found to allow selective formation of the bicyclo[4.3.0]nonyl, bicyclo[4.4.0]decyl, or bicyclo[5.4.0]-undecyl ring skeletons.

Treatment of 2-methyl-1,3,8,10-undecatetraene (**1**) with 5 mol % of triflic acid in methylene chloride at 23 °C for 2 min gave an 86% yield[4] of **2**. Protonation of **1** occurred at C-1 to produce

(1) Rohm and Haas Fellow, 1988–1989.

(2) Gassman, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 6085. Gassman, P. G.; Singleton, D. A. *J. Org. Chem.* **1986**, *51*, 3075.

(3) The various substituted tetraenes were prepared by straightforward synthetic approaches, which will be described in a full paper on this subject. Satisfactory elemental analyses and exact mass molecular weights have been obtained on all new compounds. All new compounds had IR, ¹H NMR, and ¹³C NMR spectra that were consistent with the assigned structures.

the more stable trisubstituted allyl cation **3**, which was the reactive intermediate in the formation of **2**.
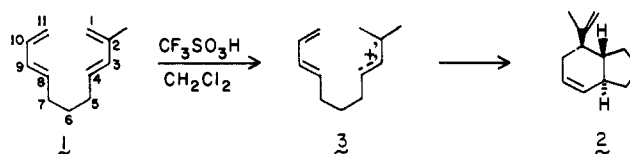
In contrast, treatment of **4** with 10 mol % of triflic acid at –23 °C for 20 min gave products that were consistent with the protonation of **4** on C_d to produce the tetrasubstituted allyl cation **5**. Subsequent *formal*[5] intramolecular Diels–Alder cyclization gave 72% of **6**, 4% of **7**, and 24% of **8** (GLC yields vs an internal standard).[6] Use of 1 equiv of the weaker methanesulfonic acid with **4** in methylene chloride at –23 °C for 2 min gave 18% of **6**, 44% of **7**, 17% of **8**, and starting material. These results suggested that **6** was a secondary product derived from **7**. Control experiments demonstrated that **7** rapidly and cleanly isomerized to **6** in the presence of triflic acid at –23 °C and that **6** was not converted into **7** under these conditions.[7]
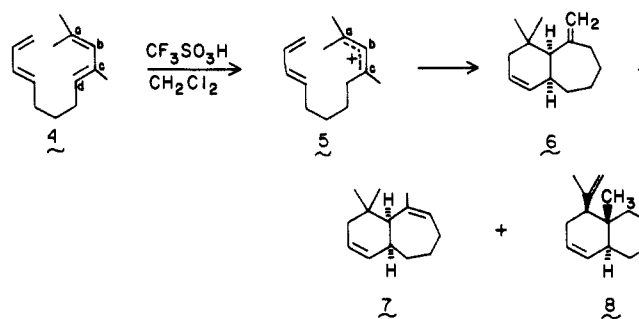
The use of *p*-toluenesulfonic acid as catalyst (100 mol %) for 40 min at 23 °C in methylene chloride also promoted the intramolecular cycloaddition reactions of **4**. Under these conditions we obtained 27% of **6**, 3% of **7**, and 41% of **8**. As a result of the change in acid catalyst and temperature, **8** had become the major product.[9–11] While this change in major product requires only a relatively small change in transition-state energies, it is particularly auspicious because **7** (and subsequently **6**) resulted from the formal addition of the a–b portion of the allyl cation of **5** to the diene while **8** resulted from the b–c portion of the allyl cation of **5** being the 2π component of the cycloaddition.

For rigorous structural assignments, **6** and **8** were each treated with excess dichlorocarbene to give the crystalline adducts **9** and **10**, respectively. Single-crystal X-ray structural determination

(4) Operating on an 81-mg scale, the yield of **2** was 86% by analytical GLC analysis vs an internal standard (undecane) and 56% by isolation by preparative GLC.

(5) The stepwise vs concerted nature of these cycloadditions is discussed in the following communication in this issue.

(6) On a 76-mg scale, **6** and **8** were isolated in 53% and 22% yields, respectively, from **4** by preparative HPLC.

(7) This is in contrast to the direction of the analogous isomerization of α-himachalene to β-himachalene.[8] Apparently, the location of the *gem*-dimethyl groups on the seven-membered rings of the himachalenes vs that on the six-membered rings of **6** and **7** results in a significant change in the conformational stability of the two analogues, with the himachalenes being more stable with the double bond endocyclic, while our system is more stable with the double bond exocyclic.

(8) Harref, A. B.; Bernardini, A.; Fkih-Tetouani, S.; Jacquier, R.; Viallefont, P. *J. Chem. Res., Synop.* **1981**, 372. Mehta, G.; Singh, B. P. *J. Org. Chem.* **1977**, *42*, 632. Challand, B. D.; Hikinko, H.; Kornis, G.; Lange, G.; de Mayo, P. *J. Org. Chem.* **1969**, *34*, 794.

(9) We have found that yields and product ratios for a variety of ionic Diels–Alder reactions are dramatically dependent on both the acid catalyst and the temperature. For additional examples, see the following communication.

(10) Control experiments demonstrated that **8** was not interconverted with either **6** or **7** under the reaction conditions.

(11) With 100 mol % of methanesulfonic acid as the catalyst, the ratio of (**6** + **7**)/**8** systematically declined as the temperature increased: –23 °C, 3.6; 0 °C, 2.4; 23 °C, 1.3; 40 °C, 0.8.