

(PP₃)Rh⁺ fragment. The latter easily re-forms the starting trigonal-bipyramidal chloride 10 by addition of (PPN)Cl. In a similar way, C-C bond formation at rhodium occurs when the σ -acyl complexes 6 and 7 are reacted in THF with the alkylating agents MeOSO₂CF₃ and EtOSO₂CF₃. Instead of the expected cis organyl acyl derivatives, CH₃COCH₃ or the asymmetric ketones C₂H₅COCH₃, CH₃COC₆H₅, and C₂H₅COC₆H₅ quantitatively form (detected by GC) together with the promptly reutilizable 16-electron (PP₃)Rh fragment.

Theoretical and structural investigations are in progress to try to rationalize the different chemistry of the closely related (np₃)Rh⁺ and (PP₃)Rh⁺ fragments. An important role in determining the behavior of these systems is certainly played by the nature of the central donor atom of the tripodal ligand, i.e. nitrogen or phosphorus. In particular, while the amine donor easily unfastens as a new, appropriate ligand approaches the metal, no evidence for P_{central}-M bond cleavage in PP₃ complexes has so far been reported.¹⁵ In addition, PP₃ is more reluctant than np₃ to form octahedral complexes. As an example, the octahedral cis dihydride [(PP₃)RhH₂]⁺ easily rearranges to the trigonal-bipyramidal η^2 -dihydrogen derivative in ambient temperature solutions whereas [(np₃)RhH₂]⁺ invariably maintains the cis dihydride structure.⁹

(15) Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* 1986, 25, 616 and references therein.

Rapid, Reversible Proton Exchange between Ring and Metal Sites in the Aryne Complexes H₂Os₃(CO)₉(μ_3 , η^2 -C₆H₄) and Related Derivatives

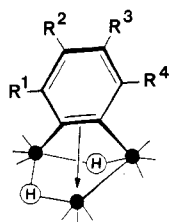
Heinz-Josef Kneuper and John R. Shapley*

Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Received July 14, 1987

Summary: ¹H NMR spin saturation transfer studies on the complexes H₂Os₃(CO)₉(μ_3 , η^2 -aryne) (aryne = C₆H₄, C₆H₃Me, and C₆H₂Me₂) at ca. 90 °C have established proton transfer between the metal hydride (Os-H-Os) sites and aryne ring (C-H) sites.

One of the intermolecular C-H bond activation reactions evidenced by the triosmium cluster system is the transformation of simple arenes into the aryne complexes H₂Os₃(CO)₉(μ_3 , η^2 -C₆H_{4-x}R_x) (e.g., see 1-3).¹ This reaction

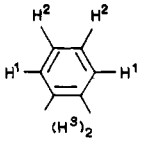
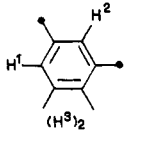
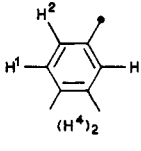
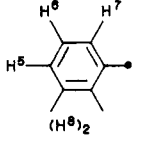


- 1: R¹ = R² = R³ = R⁴ = H
 2: R¹ = R³ = H, R² = R⁴ = Me
 3a: R¹ = R² = R⁴ = H, R³ = Me
 3b: R¹ = R² = R³ = H, R⁴ = Me

can be accomplished directly from Os₃(CO)₁₂² or under

(1) Deeming, A. J. *Adv. Organomet. Chem.* 1986, 26, 1.

Table I. Spin Saturation Transfer (SST) Experiments^a

compd ^b	site of irradiation	site of SST effect
	H ³	H ¹
	H ³	H ¹
	H ⁴ H ²	H ¹ and H ⁶ (3b) H ³ and H ⁷ (3b)
	H ⁸	H ³ (3a)

^a 500 MHz, CD₃NO₂ solution, +90 °C, PRESAT pulse sequence.⁶
^b Signal assignments based on previous work.^{2,3}

milder conditions from Os₃(CO)₁₀(NCMe)₂,³ but intermediates in this obviously multistep process have not been observed. We wish to report the first observation of rapid, reversible exchange between protons bound to the triosmium frame and those on the aryne ring. This observation, conducted by ¹H NMR spin saturation transfer, and the resulting mechanistic interpretation serve to cast light on the pathway of aryne complex formation.

The crystal structure of 1 clearly implies that the two hydride ligands occupy inequivalent edges,³ but in solution separate ¹H NMR signals are observed only at very low temperatures (<-120 °C).⁴ The effects of spin saturation transfer become apparent above ca. 80 °C (see Table I).⁵ Selective irradiation of the hydride signal in 1 shows a diminution in intensity for just one of the two sets of ring protons. The same result is seen for the dimethyl derivative 2. The situation is more informative for the monomethyl benzyne complex 3, which exists as two isomers, a major one, 3a (ca. 80%), and a minor one, 3b (ca. 20%). Selective irradiation of the hydride signal in 3a shows spin transfer not only to one of the adjacent ring protons in 3a but also to the equivalent site in 3b. Conversely, irradiating the hydride signal in 3b reveals spin transfer only to one of the adjacent ring protons in 3a. These results are uniquely consistent with a process in which the aryne

(2) (a) Deeming, A. J.; Underhill, M. J. *Organomet. Chem.* 1972, 42, C60. (b) Deeming, A. J.; Underhill, M. J. *Chem. Soc., Dalton Trans* 1974, 1415.

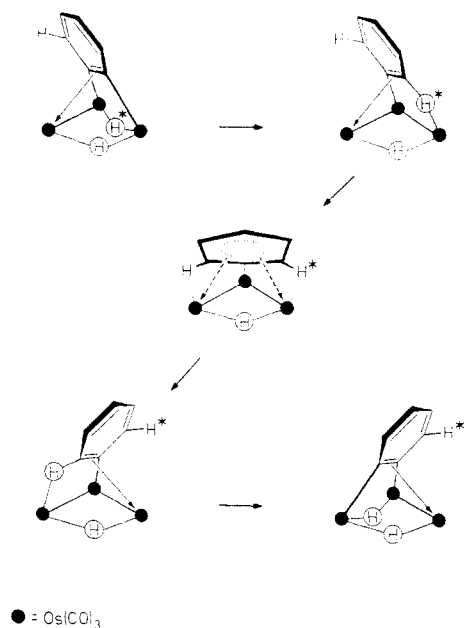
(3) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Rosales, M. F. *J. Chem. Soc., Dalton Trans.* 1983, 2257.

(4) Azam, K. A.; Yin, C. C.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* 1978, 1201.

(5) Spin saturation transfer experiments were conducted with the PRESAT pulse sequence⁶ on a GE GN-500 FT-NMR spectrometer. The appropriate signal in the ¹H NMR spectrum was irradiated selectively for a period of >5T₁, and then the FID was recorded immediately.

(6) Campbell, T. D.; Dobson, C. M.; Ratcliffe, R. G.; Williams, R. F. *P. J. Magn. Reson.* 1978, 29, 397.

Scheme I



ring attachment to the Os₃ framework shifts in 1,2 steps concomitant with proton transfer to the metal from the ring for a C-H bond being broken and from the metal to the ring for a C-H bond being formed. Thus, in particular isomer **3a** can undergo a 1,2 shift either in one direction and regenerate itself or in the opposite direction and generate isomer **3b**. However, **3b** can only step in one direction, which immediately generates **3a**. The possibility of **3a** ↔ **3b** interconversion has been mentioned previously,^{3,4} but our SST results provide direct evidence not only for the isomers **3a,b** but also for the "degenerate" cases of **1** and **2**.

We postulate the mechanism shown in Scheme I. A proton hops from a site associated with a pair of electrons between two Os atoms (Os-H-Os) to a site associated with a pair of electrons between a carbon atom and an osmium atom (C-H-Os) (an agostic⁷ three-center, two-electron bond). This is followed by rolling of the aryl moiety such that a new C-H-Os bridge is created and the former is broken. Finally, exchange is completed by proton migration back to the Os-H-Os site. Since the presence of CO atmosphere has no effect on the rate, some π-bonding between the aryl moiety and the Os₃ framework must be maintained throughout the rearrangement.

Compound **2** was chosen as the simplest case for quantitative measurements. There was no measurable NOE at the ring proton sites upon irradiation of the hydride signal, so the rate constant could be determined readily from straightforward intensity and relaxation time measurements.^{8,8} At 90 °C, the exchange rate constant $k = 0.7 \pm 0.05 \text{ s}^{-1}$, which corresponds to $\Delta G^\ddagger(363 \text{ K}) = 21.7 \pm 0.1 \text{ kcal/mol}$. This ΔG^\ddagger value is similar to that recently determined for exchange between the two types of proton sites in $\text{H}_3\text{Os}_3(\text{CO})_9(\mu_3\text{-CH})$ ($\Delta G^\ddagger = 24 \text{ kcal/mol}$),¹⁰ con-

sistent with rate-determining proton migration in both cases.

It has been suggested¹ that the pathway to benzyne complex **1** involves the formation first of a hydrido-phenyl complex with 10 CO ligands, i.e., $\text{HOs}_3(\text{CO})_{10}(\mu\text{-C}_6\text{H}_5)$, which is then followed by CO loss and the second C-H bond scission. It is likely that the type of intermediate species proposed here, i.e., $\text{HOs}_3(\text{CO})_9(\mu_3\text{-C}_6\text{H}_5)$, is the same as that involved in the latter step. Furthermore, the selective SST results for **1** rule out any rapid equilibrium with the η^6 -benzene complex $\text{Os}_3(\text{CO})_9(\mu_3, \eta^6\text{-C}_6\text{H}_6)$.¹¹ Thus, the hydrido-phenyl and benzene complexes of the Os₃(CO)₉ fragment do not readily interconvert. This contrasts with the demonstration of interconverting hydrido-phenyl and benzene complexes of a mononuclear rhodium fragment¹² but is reminiscent of the significant barrier observed between corresponding hydrido-vinyl and ethylene complexes of a mononuclear iridium center.¹³ Further SST studies of CH/OsH exchange in hydrido-triosmium hydrocarbyl complexes are in progress.

Acknowledgment. This research was supported by a National Science Foundation Grant (CHE 84-07233) to J.R.S. H.-J.K. thanks the Deutsche Forschungsgemeinschaft (Bonn) for a fellowship. The GE GN-500 FT-NMR spectrometer was purchased in part with funds from National Science Foundation Grant CHE 85-14500 to the School of Chemical Sciences at the University of Illinois.

(11) Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* 1985, 1682. **Note Added in Proof.** The Cambridge group has observed the photochemical transformation of $\text{Os}_3(\text{CO})_9(\mu_3, \eta^6\text{-C}_6\text{H}_6)$ into $\text{H}_2\text{Os}_3(\text{CO})_9(\mu_3, \eta^2\text{-C}_6\text{H}_4)$: Gallop, M. A., personal communication.

(12) Jones, W. D.; Feher, F. D. *J. Am. Chem. Soc.* 1986, 108, 4814.

(13) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* 1985, 107, 4581.

Some Interesting Properties in Silapropellanes and Derivatives. A Theoretical Study of Inverted Tetracoordinate Silicon

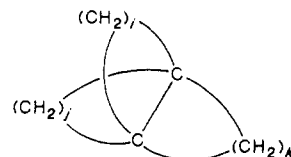
Shigeru Nagase* and Takako Kudo

Department of Chemistry, Faculty of Education
Yokohama National University, Yokohama 240, Japan

Received June 2, 1987

Summary: Ab initio calculations show that fully silicon-substituted propellanes, pentasila[1.1.1]propellane and octasila[2.2.2]propellane, are less strained than the corresponding carbon compounds and are interesting synthetic targets. Especially interesting is a drastic effect of trioxa substitution on the bridge bonding between the inverted tetracoordinate silicon atoms.

The $[i,j,k]$ propellanes, which consist of three rings fused to a common carbon-carbon bond and may be regarded as hexasubstituted ethanes, have long been the subject of much experimental and theoretical interest.¹ The pro-



(7) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* 1983, 250, 395.

(8) The T_1 value for the C-H site was determined as $T_1 = 3.99 \text{ s}$. The intensity ratio for the signal without and with irradiation of the hydride site was 3.79 ± 0.2 . From these values,⁹ $k = 0.7 \pm 0.05 \text{ s}^{-1}$. The free energy of activation from the Eyring equation is $\Delta G^\ddagger = 21.7 \pm 0.1 \text{ kcal mol}^{-1}$.

(9) Sandström, J. *Dynamic NMR Spectroscopy*; Academic: New York, 1982; Chapter 7.

(10) ValderVelde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* 1987, 26, 3077.