J. Am. Chem. Soc. 1986, 108, 334-335

Acknowledgment. We are indebted to Professor J. I. Brauman for invaluable suggestions and to K. N. Smith and D. H. Li for experimental assistance. Research was partially funded by the Department of the Army (Contract DAAG29-85-K-0242).

Mechanism of Formation of the π-Allyl Palladium Chloride Complex from Methylenecyclohexane and Palladium Chloride

Douglas R. Chrisope and Peter Beak*

Roger Adams Laboratory, School of Chemical Sciences
University of Illinois, Urbana, Illinois 61801

Received August 12, 1985

The formal insertion of palladium into the allylic carbon–hydrogen bond of an olefin to provide a π-allyl complex is of interest as a prototypical transition-metal insertion and as a source of η^3 complexes for synthesis. While there is general agreement that the first step of the mechanism involves π-complexation of palladium with the olefin,[1,2] there are at least three possibilities for the subsequent insertion. These are shown in Scheme I for $PdCl_2$ and methylenecyclohexane as (a) explicit palladium insertion into the carbon–hydrogen bond to give a palladium hydride intermediate which loses hydrogen chloride,[3] (b) removal of the hydrogen as a proton by bound chloride,[4] or (c) removal of the proton by an external base.[5] The product of this step can dimerize to give the well-characterized η^3 complexes.[1] The three mechanisms are distinguished by their transition-state geometries, which under the analysis of More O'Ferrall,[6] could be reflected in the magnitude of the deuterium isotope effect for removal of the allylic hydrogen. We wish to report evidence which suggests that (a), the most popular path, is not operative with methylenecyclohexane and that transfer of the hydrogen as a proton by (b) or (c) are consistent with our analysis.

If the geometry for intramolecular hydride abstraction by palladium in pathway (a) approximates a four-membered ring with a hydrogen-transfer angle of 90–100°, model calculations predict a k_H/k_D of 1.7–2.3 at 25 °C.[6] As a test of this prediction for palladium we have found the isotope effect for the palladium-catalyzed isomerization of methylenecyclohexane to 1-methylcyclohexene, a reaction that may involve a reversible addition of a palladium hydride species in a four-center transition state,[7] to be 1.8 ± 0.5 at 60 °C.

Scheme I

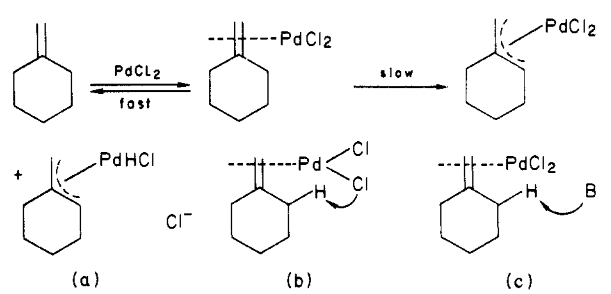


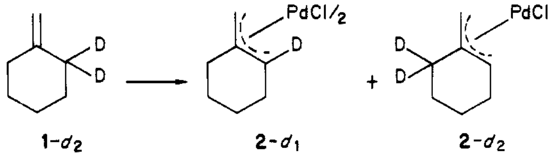
Table I. Product Isotope Effects for Conversion of **1**-d_2 to **2**-d_1 and **2**-d_2

Reaction conditions (solvent/reagents)[a]	k_H/k_D[b]
70% AcOH/$PdCl_2$ (aq), NaCl, $CuCl_2$	3.55 ± 0.1
AcOH/$PdCl_2$, NaCl, $CuCl_2$, NaOAc[c]	3.48 ± 0.1
DMF/$PdCl_2$	4.55 ± 0.1
DMF/$PdCl_2$, 21 °C	5.19 ± 0.1
DMF/$PdCl_2$, 86 °C	3.66 ± 0.1
benzene/$PdCl_2$, 2 equiv of DMF	4.32 ± 0.1

[a] Unless otherwise stated, all reactions were performed at 60 °C. [b] Analysis by GC–MS of the mixture of amines derived from **2**. [c] Conditions of Trost et al.[3c]

A model of the transition state for pathway (b), constructed by using X-ray structure data from π-olefin complexes[8] for bond lengths and angles, shows the hydrogen transfer angle to be ca. 135° in the most favorable conformation. This leads to a prediction for the isotope effect of 3.5–4.2 at 25 °C by interpolation of More O'Ferrall's model. A value of 3.0–3.5 has been reported for insertion of platinum into an alkyl carbon–hydrogen bond at 157 °C in a five-center transition state.[9] For pathway (c), proton abstraction by base should be linear and therefore display a maximum isotope effect of ca. 7 at 25 °C unless diminished by an unsymmetrical transition state.[10]

The measured isotope effects for the allylic palladation of **1**-d_2[11] to **2**-d_1 and **2**-d_2 by $PdCl_2$ are summarized in Table I. Reactions in acetic acid (AcOH) with and without sodium acetate gave isotope effects of 3.5 ± 0.1 at 60 °C. This is most consistent with pathway (b), proton removal by bonded chloride with a hydrogen-transfer angle of 120–140°, a result that is also supported by stereochemical studies.[2,12] Brief mention has been made of isotope effects in similar reactions which are near these values.[12,13]



If the reaction is carried out in dimethylformamide (DMF) or in benzene containing 2 equiv of DMF, isotope effects of 4.55 and 4.32, respectively, are observed at 60 °C and values of 3.66 and 5.19 are obtaned at 21 °C and 86 °C, respectively. These values are most consistent with a nearly linear and symmetrical transition state and suggests abstraction of the proton by an external base.[14a] The DMF could act to displace the chloride ligand which then may act as an external base.

The fact that the allylic palladation and isomerization have different isotope effects rules out rate-determining formation of a π-allyl palladium hydride species as a common intermediate for these two reactions.[7] The possibility that the observed isotope effect for the formation of **2** results from slow decomposition of

---

(1) Maitlis, P. M.; Espinet, P.; Russel, M. J. H. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. A. G., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 6, pp 386–388 and references therein.

(2) L. M. Stephenson has observed an isotope effect of 3.3 in an intermolecular and intramolecular competition involving the 2,3-dimethyl-2-butenes. L. M. Stephenson, lecture at the Mechanism Conference, Durham, NC, June 1984, and private communication to us. In the present case, the rapid and reversible formation of a π-olefin complex is consistent with a kinetic isotope effect of 4.5 ± 1 observed for **1** and **1**-d_4 in DMF solvent which is within experimental error of the value obtained for **1**-d_2 under the same conditions.

(3) (a) Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1969**, *87*, 225. (b) Collman, J. P.; Hegedus, L. S. "Principles of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 680. (c) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *Am. Chem. Soc.* **1978**, *100*, 3407.

(4) Lukas, J.; Coren, S.; Blom, J. E. *J. Chem. Soc., Chem. Commun.* **1969**, 1303.

(5) Ketley, A. D.; Braatz, J. *J. Chem. Soc., Chem. Commun.* **1968**, 169.

(6) More O'Ferrall, R. A. *J. Chem. Soc.* B **1970**, 785.

(7) Jira, R.; Freiesleben, W. In "Organometallic Reactions"; Becker, E. I., Tsutsui, M., Eds.; Wiley: New York, 1972; Vol. 3, (a) p 133, (b) p 136.

(8) (a) Holden, J. R.; Baenziger, N. C. *J. Am. Chem. Soc.* **1955**, *77*, 4987. (b) Dempsey, J. N.; Baenziger, N. C. *Ibid.* **1955**, *77*, 4984.

(9) Foley, P.; Whitesides, G. M. *Ibid.* **1979**, *101*, 2732.

(10) Reaction within dimers which could remove the angular constraints of (a), (b), or (c) appear geometrically difficult. Until further information is available the present test is considered to be applied to monomers.[1-5]

(11) Beak, P.; Berger, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 3848.

(12) Harvie, I. J.; McQuillin, F. J. *J. Chem. Soc. Chem. Commun.* **1978**, 747. See also: Collins, D. J.; Jackson, R.; Times, R. N. *Aust. J. Chem.* **1980**, *33*, 2663.

(13) A product isotope effect of 1.3 in the reaction of isobutene containing a single allylic deuterium atom with $PdCl_2$/NaCl/NaOAc in AcOH has been reported: Lukas, J.; Ramakers-Blom, J. E.; Hewitt, T. G.; de Boer, J. J. *J. Organomet. Chem.* **1972**, *46*, 167. Statistical correction factor allows derivation of a k_H/k_D value of 3.9.

(14) Melander, L.; Saunders, W. H. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980; (a) p 157, (b) p 144.

0002-7863/86/1508-0334$01.50/0

a Pd–H intermediate is unlikely since isotope effect determinations in metal–hydride bond cleavage by external species give values of 0.4 at 65–100 °C.[15] The assumption that there is no significant contribution of tunneling to the observed isotope effects is established by plots of log k_H/k_D vs. $1/T$ which have slope and intercept corresponding to ΔE_a and A_H/A_D of 1.075 kcal and 0.844, respectively.[14b]

In summary, the present isotope effects, if analyzed under the model of More O'Ferrall, suggest that the formal insertion of palladium into the allylic carbon–hydrogen bond of methylenecyclohexane proceeds by removal of the hydrogen as a proton by a base which can be either internal or external to the palladium complex. The use of this information for improved preparation of (π-allyl)palladium complexes and the extension of this mechanistic approach to other insertions is under study.

Acknowledgment. We are grateful to the National Science Foundation for support of this work, to Professor L. M. Stephenson for information about work in his laboratory, and to Professor Jack Halpern for a helpful discussion.

---

(15) (a) Sweany, R.; Butler, S. C.; Halpern, J. *J. Organomet. Chem.* **1981**, *213*, 487. (b) Sweany, R.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 1835.

Preparation of the First Molecular Carbon Monoxide Complex of Uranium, $(Me_3SiC_5H_4)_3UCO$

John G. Brennan,† Richard A. Andersen,*† and
John L. Robbins‡

*Chemistry Department and Material and Molecular
Research Division of Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720 and
Exxon Research and Engineering Company
Clinton Township, Route 22 East
Annandale, New Jersey 08801*

Received September 30, 1985

Migratory insertion of an anionic group onto coordinated carbon monoxide or an isocyanide is an important mechanistic postulate in organoactinide chemistry.[1] In contrast to transition metals, where carbon monoxide complexes abound, only three examples of carbon monoxide coordination to uranium have been observed in matrix isolation studies at cyrogenic temperatures. These studies showed that $U(CO)_6$ can exist below ca. 20 K and that ν_{CO} of 1961 cm^{-1} is similar to that found for $W(CO)_6$, ν_{CO} is 1987 cm^{-1} under similar conditions.[2a,b] The ν_{CO} is lowered substantially from gaseous CO (ν = 2145 cm^{-1}) which implies that uranium metal is a π-donor, though the bonds are either kinetically labile, thermodynamically weak, or both. In $UF_4(CO)$ the ν_{CO} of 2182 cm^{-1} at 20 K[2c] shows that the tetravalent compound does not engage in π-back-bonding to CO.[3] In another study, UO_2 has been shown to absorb CO at temperatures below 20 K; the CO stretching frequency was not measured.[2d] In this paper, we give evidence for $(Me_3SiC_5H_4)_3UCO$, the first molecular actinide complex of carbon monoxide, in solution and solid phase.

We have determined, on the basis of equilibrium constant measurements, that the ligand displacement series toward $(MeC_5H_4)_3U$ is $PMe_3 \approx P(OMe)_3$ > pyridine > tetrahydrothiophene > tetrahydrofuran and toward $(Me_3SiC_5H_4)_3U$ the series is EtNC > EtCN.[4a] The observation that phosphite and isocyanide ligands, which are generally classified as π-acceptor ligands,[4b] are good ligands toward the trivalent uranium metallocenes suggests that the uranium center can act as a π-donor. The extent of π-acceptance is difficult to judge on the basis of the infrared spectrum[5] as ν_{CN} of 2160 cm^{-1} in $(Me_3SiC_5H_4)_3UCNEt$[6a] is slightly higher in energy than that in free CNEt of 2151 cm^{-1}. In Cp_3UCN(cyclohexyl),[6c] ν_{CN} increases by 25 cm^{-1} on coordination. The purported π-base character of $(RC_5H_4)_3U$ led us to expose $(Me_3SiC_5H_4)_3U$ to one of the best π-acids known, carbon monoxide.

The deep green solution of $(Me_3SiC_5H_4)_3U$ in either pentane or hexane turned burgundy on exposure to carbon monoxide at 1 atm and 20 °C. Volumetric studies showed that the metallocene absorbs 1.0 ± 0.05 M equivalents of carbon monoxide at 25 °C. Exposure of the burgundy carbon monoxide complex to vacuum or purging the solution with argon regenerates the green, carbon monoxide free $(Me_3SiC_5H_4)_3U$. The carbon monoxide, vacuum cycle may be repeated several times without detectable decomposition. In addition, the burgundy solution may be stored for at least 2 years at −80 °C. Clearly, $(Me_3SiC_5H_4)_3U$ reversibly adsorbs a molar equivalent of carbon monoxide in hydrocarbon solution. Examination of the infrared spectrum of the burgundy solution using ^{12}CO shows ν_{CO} at 1976 cm^{-1}, with ^{13}CO ν_{CO} is 1935 cm^{-1}, and with $C^{18}O$ ν_{CO} is 1932 cm^{-1}. The predicted values for ν ^{13}CO and $C^{18}O$ are 1931 and 1930 cm^{-1}, respectively.[7]

The $(Me_3SiC_5H_4)_3U$ also reversibly absorbs ^{12}CO in the solid state. Exposure of $(Me_3SiC_5H_4)_3U$ in a KBr wafer to ^{12}CO at 1 atm results in the appearance of an absorption at 1969 cm^{-1} which completely disappears when the sample is evacuated for 1.5 h. Using ^{13}CO (99%) causes the absorption to shift to 1922 cm^{-1}.

We assume that the complex is carbon-bonded, as are all CO complexes, and the U–C–O unit is linear. Some support for this is derived from the X-ray crystal structure determination of $(Me_3SiC_5H_4)_3UCNEt$.[8] The averaged U–C(Cp) distance is 2.81 ± 0.03 Å, the U–Cp ring centroid distance is 2.53 Å, the U–C(CNEt) distance is 2.57 (3) Å, the ring centroid–U–ring centroid angle is 118.6°, the ring centroid–U–C(CNEt) angle is 97°, and, most importantly, the U–C–N angle is 173.6 (2.0)° and the C–N–C (Et) angle is 170.2 (2.6)°.

A very crude molecular orbital model, based upon the symmetry orbitals, may be constructed that accounts for the reduction in the C–O stretching frequency in the complex. Assume that the molecule has C_{3v} symmetry. The e_1 and a pπ SALC'S for $(Cp)_3$ transform as $2a_1 + a_2 + 3e$. In C_{3v} symmetry the metal AO's transform as $a_1[s, z, z^2, z^3, x(x^2 - 3y^2)]$, $a_2[y(3x^2-y^2)]$, and $e[x, y, x^2 - y^2, xy, xz, yz, xz^2, yz^2, xyz$, and $z(x^2 - y^2)]$. If we let the nine Cp orbitals overlap with the available metal AO's then we have left over $3a_1 + 2e$ symmetry orbitals that contain three electrons to overlap with the filled σ-orbitals and the empty π-

---

† Chemistry Department, University of California at Berkeley.

‡ Exxon Research and Engineering Co.

(1) (a) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, V. W.; Vollmer, S. H.; Day, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 5393–5396. (b) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063–4066. (c) Kramer, R. E.; Maynard, R. B.; Paw, J. C.; Giljie, J. W. *Organometallics* **1982**, *1*, 869–871. (d) Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484–3491. (e) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051–7064 and references therein. (f) Dormond, A.; Elbouadili, A. A.; Moise, C. *J. Chem. Soc., Chem. Commun.* **1984**, 749–751. (g) Zanella, P.; Paolucci, G.; Rossetto, G.; Benetollo, F.; Polo, A.; Fischer, R. D.; Bombieri, G. *J. Chem. Soc., Chem. Commun.* **1985**, 96–98.

(2) (a) Slater, J. L.; Sheline, R. K.; Lin, K. C.; Welter, W. *J. Chem. Phys.* **1971**, *55*, 5129–5130. (b) Sheline, R. K.; Slater, J. L. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 309–316. (c) Kunze, K. R.; Hauge, R. H.; Hamill, D.; Margrave, J. L. *J. Phys. Chem.* **1977**, *81*, 1664–1667. (d) Roberts, L. E. J. *J. Chem. Soc.* **1955**, 3939–3946. Lanthanide metals[2e] and lanthanide trifluorides[2f] give complexes with CO in cyrogenic matrices. (e) Slater, J. L.; DeVore, T. C.; Calder, V. *Inorg. Chem.* **1973**, *12*, 1918–1921. (f) Hauge, R. H.; Gransden, S. E.; Margrave, J. L. *J. Chem. Soc., Dalton Trans.* **1979**, 745–747.

(3) Tatsumi, K.; Hoffman, R. *Inorg. Chem.* **1984**, *23*, 1633–1634.

(4) (a) Brennan, J. G., unpublished results. (b) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapter 3.

(5) (a) Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1977**, *16*, 963–964. (b) Beach, D. B.; Jolly, W. L. *Ibid.* **1985**, *24*, 567–570.

(6) (a) Red crystals of $(Me_3SiC_5H_4)_3U(CNEt)$ can be isolated from the reaction of $(Me_3SiC_5H_4)_3U$[5b] and the isocyanide in hexane, mp 112–115 °C. Anal. Calcd for $C_{27}H_{44}NSi_3U$: C, 46.0; H, 6.29; N, 1.99. Found: C, 45.9; H, 6.31; N, 1.93. (b) Brennan, J. G.; Andersen, R. A.; Zalkin, A., unpublished results. (c) Kanellakopulos, B.; Fischer, E. O.; Dornberger, E.; Baumgartner, F. *J. Organomet. Chem.* **1970**, *24*, 507–514.

(7) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: New York, 1975; p 36.

(8) The details are given in the supplementary material.

0002-7863/86/1508-0335$01.50/0