Strong evidence for cyanide binding at the Ni site is provided by the complete conversion of the $S = {}^3/_2$ $[NiFe_3S_4]^+$ EPR spectrum to a new resonance, $g = 4.4$, 3.7, and 1.9, on addition of a 50-fold excess of potassium cyanide, Figure 1c. In contrast, the EPR and low-temperature magnetic circular dichroism spectra of the $S = {}^3/_2$ $[Fe_4S_4]^+$ centers in this Fd were unaffected by the addition of a 50-fold excess of potassium cyanide (data not shown). The g values of the cyanide-bound $[NiFe_3S_4]^+$ cluster are indicative of an axial $S = {}^3/_2$ species ($E/D = 0.06$), and temperature-dependence studies (4–15 K) show that this resonance arises exclusively from the lower Kramers doublet, i.e., $D > 0$.

On the basis of the available spectroscopic data, it is not possible at the present time to determine if a similar $[NiFe_3S_4]^+$ cluster constitutes the active site of CO dehydrogenases. Ill-defined $S = {}^3/_2$ EPR signals centered around $g = 5$ are apparent in both dithionite- and CO-reduced samples of *C. thermoaceticum* CO dehydrogenase,[12] in addition to the novel $S = {}^1/_2$ resonance, $g_\parallel = 2.03$ and $g_\perp = 2.07$, that is only observed on CO reduction.[1] Moreover, it is important to note that the $S = {}^1/_2$ resonance is a relatively minor component, typically accounting for 0.15 spins/Ni.[12] EPR signals near $g = 4.3$ from a $S > {}^1/_2$ center as well as a $S = {}^1/_2$ resonance, $g = 2.04$, 1.90, and 1.71, have been assigned to the NiFe center in *R. rubrum* CO dehydrogenase.[4] Clearly, the results reported herein call for more detailed characterization of the low-field EPR signals in CO dehydrogenases. The spectroscopic consequences of binding other ligands, including CO, to the $[NiFe_3S_4]^+$ cluster in *P. furiosus* Fd are currently under investigation in this laboratory.

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Registry No. CO, 630-08-0; CO dehydrogenase, 64972-88-9; acetyl-CoA synthase, 9012-31-1.

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(12) (a) Zambrano, I. C. Ph.D. Dissertation, 1986, Louisiana State University. (b) Lindahl, P. A.; Münck, E.; Ragsdale, S. W. *J. Biol. Chem.* **1990**, *265*, 3873–3879.

Reduction of an Electronically Unsaturated Transition-Metal η^2-Acyl Complex. Arene Formation from Deoxygenative Acyl Coupling with a Cyclopentadienyl Ligand

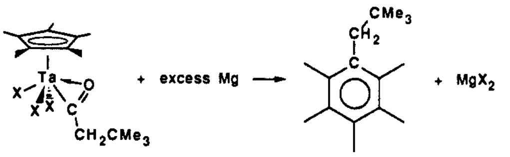
Tara Y. Meyer and Louis Messerle*

Department of Chemistry, The University of Iowa
Iowa City, Iowa 52242

Received August 21, 1989

η^2-Acyl ligands are common products from carbonylation of early-transition-metal, lanthanide, and actinide alkyls[1] and have been studied primarily from a synthetic or structural rather than a reactivity perspective. Reactions of η^2-acyls include insertion into aryl C–H bonds[2–4] and conversion into metal-bound enolates,[5–7] ketenes,[8] carboxylates,[9] ketones,[10] and mononuclear and dinuclear enediolates.[11] There are interesting reports of η^2-acyl C–O bond cleavage, including formal O atom abstraction to generate metal carbynes,[12] CO deoxygenation/cyclopentadiene synthesis following CO insertion/ring expansion into metallacyclo-3-pentene complexes[13] (which may proceed through an acyl intermediate), and generation of hexaalkylbenzenes from a $(C_5Me_5)_2Ti(III)$ acyl upon reaction with $Cp_2Mo_2(CO)_6$.[14] Our interests in mid-valent, mono(η-C_5R_5) early-metal chemistry[15,16] and in the comparative structure/reactivity of organometallic functional groups in complexes with different metal valencies led us to examine whether an electronically unsaturated η^2-acyl complex would deinsert, rearrange to a ketene hydride,[17] have altered η^2-interaction and reactivity, or undergo structural rearrangement upon reduction. We have discovered an example of the latter, specifically that η^2-acyl reduction can lead to deoxygenative coupling with a cyclopentadienyl C_{ring}–C_{ring} bond.

The η^2-acyl complex (η-C_5Me_4R)$Ta[C(O)CH_2CMe_3]Cl_3$ (**1**; R = Me, Et),[4,18,19] which is to our knowledge the most structurally distorted[18b] transition-metal η^2-acyl, is reduced by Mg, Na/Hg, K/Hg, Zn, or sodium naphthalenide in a variety of solvents to a dark orange solution, from which the arene $C_6Me_5(CH_2CMe_3)$ can be sublimed after centrifugation or filtration (eq 1). The



(1)

highest yields (61% isolated, 75% GC based on **1**) are obtained with 4 equiv of Mg in Et_2O. The arene GC yield decreases to 50% with 2 equiv of Mg or 1, 2, or 4 equiv of Na/Hg, while 0.5 equiv of Na/Hg resulted in ca. 23% GC yield. The other reductants behaved similarly but produced lower arene yields. The arene was identified by ^1H and ^{13}C NMR spectroscopy, mass spectrometry,[20] and X-ray diffraction.

The tantalum-containing product(s) are presently unidentified because of the difficulty in direct separation from byproducts or separation via derivatization. Characterization of the tantalum product(s) has been hampered by a concurrent, slow ($\tau_{1/2}$ = 1–2 days in the absence of reductant) decomposition of the starting

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(1) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059–1079.

(2) Evans, W. J.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1722–1723.

(3) Fanwick, P. E.; Kobriger, L. M.; McMullen, A. K.; Rothwell, I. P. *J. Am. Chem. Soc.* **1986**, *108*, 8095–8097.

(4) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149–164.

(5) 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.

(6) Maata, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 3576–3578.

(7) (a) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 5250–5252. (b) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194–195 and references therein.

(8) (a) Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 5499–5500. (b) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068–2070. (c) Messerle, L. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1979.

(9) Bonnesen, P. V.; Yau, P. K. L.; Hersh, W. H. *Organometallics* **1987**, *6*, 1587–1590.

(10) (a) Waymouth, R. M.; Clauser, K. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 6385–6387. (b) Waymouth, R. M.; Grubbs, R. H. *Organometallics* **1988**, *7*, 1631–1635. (c) Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 7952–7959.

(11) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127.

(12) (a) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925–931. (b) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786–2792.

(13) (a) Blenkers, J.; de Liefde Meijer, H. J.; Teuben, J. H. *Organometallics* **1983**, *2*, 1483–1484. (b) Hessen, B.; Blenkers, J.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1989**, *8*, 2809–2812.

(14) De Boer, E. J. M.; De With, J. *J. Organomet. Chem.* **1987**, *320*, 289–293.

(15) (a) Ting, C.; Messerle, L. *J. Am. Chem. Soc.* **1987**, *109*, 6506–6508. (b) Ting, C.; Messerle, L. *J. Am. Chem. Soc.* **1989**, *111*, 3449–3450. (c) Ting, C.; Messerle, L. *Inorg. Chem.* **1989**, *28*, 171–173.

(16) Messerle, L. *Chem. Rev.* **1988**, *88*, 1229–1254.

(17) Bruno, J. W.; Fermin, M. C.; Halfon, S. E.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 8738–8740.

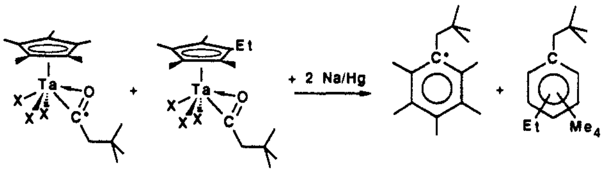
(18) (a) Meyer, T. Y.; Messerle, L. Abstracts, Third Chemical Congress of North America, Toronto, Canada, June 9, 1988; INOR 583. (b) Meyer, T. Y.; Garner, L. R.; Baenziger, N. C.; Messerle, L. *Inorg. Chem.*, in press.

(19) Rocklage, S. M. Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1982, pp 170–176.

(20) (a) ^1H NMR (δ, C_6D_6): 0.93 (s, 9, CMe_3), 2.12 (s, 9, arene Me, Me′), 2.20 (s, 6, arene Me″), 2.80 (s, 2, CH_2). ^{13}C NMR (δ, {^1H}): 16.9, 17.2, 19.3 (arene Me's), 30.4 (CMe_3), 34.6 (CMe_3), 41.3 (CH_2), 132.1, 132.4, 133.2 (arene-ring carbons), 133.9 (CCH_2CMe_3). MS (m/e): 218 (P^+), 161 ($P^+ - CMe_3$). (b) The ^1H and ^{13}C NMR data match the data reported in the literature.[18c] (c) Hallden-Abberton, M.; Engelman, C.; Fraenkel, G. *J. Org. Chem.* **1981**, *46*, 538–546.

acyl **1**, which produces, among other organics, $HC(O)CH_2CMe_3$ and a ditantalum monoacyl complex, which itself reduces to a variety of products. This decomposition prevents unambiguous determination of the reduction stoichiometry since the reduction rate of **1** decreases relative to the decomposition of **1** at low levels of reductant. An IR spectrum of the reaction mixture containing the tantalum product(s) shows broad Ta–O–Ta modes at 829 and 719 cm^{-1} and a broad O–H mode at ~3250 cm^{-1}.

Reduction of the [^{13}C]acyl $(C_5Me_5)Ta[^{13}C(O)CH_2CMe_3]Cl_3$ yielded $(CMe)_5(^{13}CCH_2CMe_3)$, establishing that the unique arene ring carbon is derived from the acyl. At least two (by GC) of the three arene isomers $(CMe)_4(CEt)(CCH_2CMe_3)$ were obtained from $(C_5Me_4Et)Ta[C(O)CH_2CMe_3]Cl_3$ reduction. A double label crossover experiment with labeled acyl and C_5R_5 groups supports a predominantly intramolecular mechanism for this unusual transformation. Reduction of an equimolar mixture of $(C_5Me_5)Ta[^{13}C(O)CH_2CMe_3]Cl_3$ and $(C_5Me_4Et)Ta[^{12}C(O)CH_2CMe_3]Cl_3$ in toluene gave the direct arene products $(CMe)_5(^{13}CCH_2CMe_3)$ and $(CMe)_4(CEt)(^{12}CCH_2CMe_3)$ in 93% relative yield (eq 2), with only 7% combined cross-product arenes, $(CMe)_5(^{12}CCH_2CMe_3)$ and $(CMe)_4(CEt)(^{13}CCH_2CMe_3)$ isomers, observed by mass spectrometry.[21]



(2)

While a complete mechanism cannot yet be proposed, several experiments have yielded pertinent mechanistic information about this intramolecular reaction. No organic or inorganic intermediates are visible by ^1H or ^{13}C NMR or IR spectroscopies during the reduction, and small molecule traps (H_2, CO, C_2H_4) do not affect the course of the reaction. The acyl/alkylidyne attack on the C_5Me_5 ring is highly selective, as there is no evidence for products from formal alkylidyne insertion into the C_{ring}–C_{methyl} or methyl C–H bonds. The ketone $C_5Me_5C(O)CH_2CMe_3$,[14] potentially derived from acyl migration to the C_5Me_5 ring, is not a free intermediate since (1) ≤0.5% can be found by GC of the reaction mixture and (2) it is not visible during in situ NMR or IR spectral studies of the reduction. The lack of intermediates that are sufficiently long-lived to be detected or trapped during the reaction suggests the possibility of a concerted intramolecular process. Mechanistic possibilities include oxycarbenoid/carbenium[22] addition to the C_{ring}–C_{ring} bond (with opening of the cyclopropyl to the arene) or acyl migration to the ring to form a lower valent $C_5Me_5C(O)CH_2CMe_3$ complex which is deoxygenated rapidly by the electrophilic tantalum. The role of the added electron(s) is presently unknown. While the LUMO in d^0 $Cp_2Ti[\eta^2\text{-}C(O)CH_3]Cl$ is primarily C–O π^* in character,[22] the assignment of the LUMO in mono(η-C_5R_5) d^0 η^2-acyl complexes awaits extended Hückel and Fenske–Hall calculations.

The synthetic utility of reductive metal acyl deoxygenation and addition to other organic ligands will be addressed after more thorough studies are completed. In conclusion, our studies show that reductive acyl deoxygenation is possible and suggest that other organometallic ligands may exhibit unusual chemistry as the metal valency is formally altered.

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Supplementary Material Available: A description of a representative acyl reduction/arene isolation experiment and crystal data, measurement conditions, refinement details, and an ORTEP diagram of the molecular structure of $C_6Me_5(CH_2CMe_3)$ (2 pages). Ordering information is given on any current masthead page.

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[21] This result was shown by MS on the arene products. Control experiments showed that (1) acyl/cyclopentadienyl scrambling between the reactants does not occur in solution and (2) arene alkylidyne scrambling does not occur under mass spectrometric conditions.

[22] Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440–4451.

Isomerization of the Cubane Radical Cation to the Bridged 1,4-Bishomobenzene (Bicyclo[3.3.0]octa-2,6-diene-4,8-diyl) Radical Cation†

X.-Z. Qin and A. D. Trifunac*

Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

P. E. Eaton and Y. Xiong

Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

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The electronic structure and the interconversion of the radical cations of the $(CH)_8$ group have recently attracted attention.[1-4] Among the $(CH)_8$ hydrocarbons, cubane[5] has high symmetry (O_h) and the highest strain energy.[6] Its physicochemical properties continue to attract experimental and theoretical interest.[6-10] The cubane radical cation (**1**) was first studied in neon matrices at 4 K.[1] The observed nonet EPR spectrum ($|A_{8H}|$ = 3.2 G) was explained by invoking a dynamic Jahn–Teller distortion of **1**. Because of the narrow temperature range of neon matrices, further reactions of **1** were not observed.[1] Here we report isomerization of **1** to the bridged 1,4-bishomobenzene radical cation (**2**), which was first demonstrated to be formed by the ring-opening of the semibullvalene radical cation.[3] A mechanism of this novel thermal rearrangement is suggested. Another highly strained compound in the $(CH)_8$ hydrocarbon family is cuneane.[11] We show here that radiolytic oxidation of cuneane also yields **2**.

1 was generated by the radiolytic oxidation[12] of cubane in three Freon matrices ($CFCl_3$, CF_3CCl_3, and $CF_2ClCFCl_2$). Similar spectra of **1** were obtained in all three matrices. Figure 1a shows the EPR spectrum of **1** in $CF_2ClCFCl_2$ at 77 K. It is a broad

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(1) Knight, L. B., Jr.; Arrington, C. A.; Gregory, B. W.; Cobranchi, S. T.; Liang, S.; Paquette, L. *J. Am. Chem. Soc.* **1987**, *109*, 5521.

(2) Gerson, F.; de Meijere, A.; Qin, X.-Z. *J. Chem. Soc., Chem. Commun.* **1989**, 1077.

(3) Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1990**, *112*, 2835.

(4) Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1990**, *112*, 2837.

(5) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157.

(6) Hassenrück, K.; Martin, H.-D.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125.

(7) Bischof, P.; Eaton, P. E.; Gleiter, R.; Heilbronner, E.; Jones, T. B.; Musso, H.; Schmelzer, A.; Stober, R. *Helv. Chim. Acta* **1978**, *61*, 547.

(8) Della, E. W.; McCoy, E. F.; Patney, H. K.; Jones, G. L.; Miller, F. A. *J. Am. Chem. Soc.* **1979**, *101*, 7441.

(9) Gassman, P. G.; Yamaguchi, R. *Tetrahedron* **1982**, *38*, 1113.

(10) Pine, A. S.; Maki, A. G.; Robiette, A. G.; Krohn, B. J.; Watson, J. K. G.; Urbanek, T. *J. Am. Chem. Soc.* **1984**, *106*, 891.

(11) Hassenrück, K.; Martin, H.-D.; Mayer, B. *Chem. Ber.* **1988**, *121*, 373.

(12) Shiotani, M. *Magn. Reson. Rev.* **1987**, *12*, 333.

0002-7863/90/1512-4565$02.50/0