This may be explained by experimental errors in measuring very small values. In any case the $^{36-32}S$ value for **5** is compatible only with the values for singly bonded S in the model compounds.

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Facile Stereospecific Synthesis of a Dihydroxyindenoindene Unit from an Alkyne and CO via Samarium-Mediated CO and CH Activation[1]

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We have recently reported that the low-valent samarium complex $(C_5Me_5)_2Sm(THF)_2$ (I)[3] has the capacity to assemble three CO molecules into a dimetal-substituted ketenecarboxylate unit in $[(C_5Me_5)_4Sm_2(O_2CCCO)(THF)]_2$.[4] This remarkable transformation, in which one CO loses its oxygen as it is homologated, suggests that considerable reactivity is available in the samarium/CO reaction system. We were interested in utilizing this reactivity to functionalize hydrocarbon substrates with CO and we report here the results of a reaction with an alkyne substrate.

Complex I reacts with $C_6H_5C{\equiv}CC_6H_5$ to form a compound identified as $[(C_5Me_5)_2Sm]_2C_2(C_6H_5)_2$ (II) by elemental and chemical analysis.[5] II may have an enediyl structure: $[(C_5Me_5)_2Sm](C_6H_5)C{=}C(C_6H_5)[Sm(C_5Me_5)_2]$.[6] The black II (141 mg, 0.14 mmol) reacts with CO at 90 psi over a 1-day period in 20 mL of hexane in a 3-oz Fischer-Porter aerosol reaction vessel to form a brown-red solution from which yellow-orange crystals (III, 105 mg) are obtained. III was isolated by filtration in a glovebox and characterized by complexometric metal analysis and ^1H NMR and IR spectroscopy.[7]

These data did not specify the identity of III and an X-ray structural determination was carried out.[9] The diffraction data identified III as $[(C_5Me_5)_2Sm]_2(O_2C_{16}H_{10})$, which has the structure shown in Figure 1. The ^1H NMR spectrum of the solution from which III was obtained showed that III was the major product of the reaction giving an overall yield of 70%.[10]

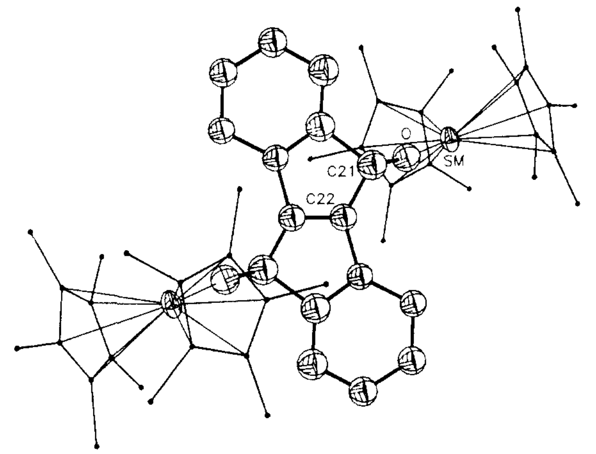
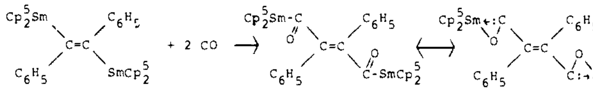


Figure 1. ORTEP plot of the molecular structure of $[(C_5Me_5)_2Sm]_2O_2C_{16}H_{10}$ with C_5Me_5 carbon atoms represented as dots for clarity. Sm′ is above the plane of the dihydroxyindenoindene ligand; Sm is below. Selected bond distances (Å) and angles include: Sm–C(ring) av, 2.70 (3); Sm–O, 2.08 (2); (ring centroid)–Sm–(ring centroid), 139.85°; Sm–O–C21, 173 (2)°; C21–O, 1.43 (4); C(22)–C(22)′, 1.25 (5); C(21)–C(22), 1.46 (4).

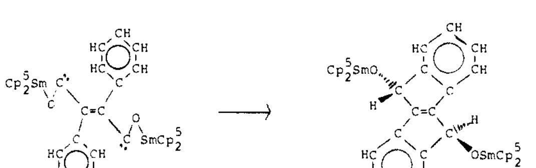
The hydrocarbon fragment in $[(C_5Me_5)_2Sm]_2(O_2C_{16}H_{10})$ can be removed by reduction with sodium in THF. Removal of THF from this mixture and extraction with hexane gave 5,10-dihydroindeno[2,1-*a*]indene identified by MS and NMR spectroscopy.[11]

The structure of III indicates that two molecules of CO have been condensed with one molecule of diphenylethyne to form a tetracyclic dihydroindenoindene unit.[12] Hence, the six-membered rings in Figure 1 have C–C distances characteristic of aromatic rings in fused polycyclic hydrocarbon systems[13] and the C22–C22′ connection is formally a double bond.[14] C21 and C21′ have angles consistent with sp^3 hybridization. The hydrogen atoms on these carbon atoms were not located in the X-ray study. C21 and C21′ are substituted in an exclusively trans manner with $OSm(C_5Me_5)_2$ groups.

The formation of III can be rationalized by successive CO insertion and C–H activation steps on the precursor II as shown in eq 1 and 2 ($Cp^5 = C_5Me_5$). CO insertion into lanthanide carbon



(1)



(2)

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(1) Reported in part at the "190th National Meeting of the American Chemical Society," Chicago IL, Sept 1985.

(2) (a) Alfred P. Sloan Research Fellow. (b) University of California—Irvine. (c) University of Alabama.

(3) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

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(6) ^1H and ^{13}C NMR spectra are consistent with this structure. Hydrolysis gives *trans*-stilbene. A crystallographically characterized azobenzene analogue has this structure.

(7) Anal. Calcd for $[(C_5Me_5)_2Sm]_2O_2C_{16}H_{10}$: Sm, 27.98. Found: Sm, 25.1. ^1H NMR (C_6D_6, 5.58 mM) δ 8.99 (1 H), 1.53 (30 H, C_5Me_5). Resonances attributable to the aryl protons were observed but could not be definitively assigned. The δ 8.99 absorbance is consistent with hydrogen on a carbon bonded to an O–Sm group as previously reported for $\{(C_5Me_5)_2[(C_6H_5)_3PO]Sm\}_2(\mu\text{-}OCH{=}CHO)$.[8] IR (KBr) 2900 s, 2850 s, 1600 m, 1440 s, 1375 m, 1285 s, 1170 vs, 1150 s, 1120 vs, 1020 s, 880 w, 850 vw, 800 vw, 750 sh, 740 s, 680 m.

(8) Evans, W. J.; Grate, J. W.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 1671–1679.

(9) The space group is $P2_1/n$ with $a = 15.031$ (6) Å, $b = 9.895$ (6) Å, $c = 17.273$ (5) Å, $\beta = 103.97$ (5)°, and $Z = 2$ for $D_{calcd} = 1.33$. Least-squares refinement on the basis of 1470 observed reflections converged to a final $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.066$. Hydrogen atoms were not included and the carbon atoms were refined with isotropic temperature factors. The thermal motion of the other atoms was dealt with anisotropically.

(10) Additional III is present in the hexane solution along with some diphenylethyne. III can also be isolated as a THF adduct.

(11) ^1H NMR (acetone-d_6) δ 7.560 (d, 2 H), 7.488 (d, 2 H), 7.329 (t, 2 H), 7.205 (t, 2 H), 3.683 (s, 4 H). Mass spectrum calcd for $C_{16}H_{12}$ 204.0939, found 204.0927. Uyehara, T. D.; Honda, T.; Kitahara, Y. *Chem. Lett.* **1977**, *10*, 1233–1236.

(12) The organic unit in samarium complex III is formally named a *trans*-5,10-dihydroindeno[2,1-*a*] 5,10-diolate.

(13) Matsuzaki, T. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2060–2061. Otaka, Y.; Marumo, F.; Saito, Y. *Acta Crystallogr., Sect. B* **1971**, *B27*, 2195–2199. Boyko, E. R.; Vaughan, P. A. *Acta Crystallogr.* **1964**, *17*, 152. Trotter, J.; Mak, T. C. W. *Acta Crystallogr.* **1963**, *16*, 1032. *Mol. Struct. Dimens.* **1972**, *A1*, 157, 167.

(14) Primed atoms are related to unprimed atoms by a center of inversion which is in the center of the C(22)–C(22)′ bond.

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bonds as shown in eq 1 has been previously demonstrated for $(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$.[15] The spectroscopic properties of that product, $(C_5H_5)_2Lu(\eta^2\text{-}COCMe_3)$, are consistent with a η^2-acyl ligand in which the carbon has substantial carbene or carbenium[16] character.[15] C–H addition to an adjacent carbene center as shown in eq 2 is also a precedented reaction.[17] Since this route is based on an assumed structure for II,[5,6] other mechanisms for forming III are quite possible.

The availability of substituted alkynes as synthetic precursors suggests this low-valent samarium-based alkyne CO condensation reaction could be of general use in the synthesis of polycyclic hydrocarbons. The generality of this system is under study.

Acknowledgment. We thank the National Science Foundation for support of this research and the Alfred P. Sloan Foundation for a Research Fellowship (to W.J.E.).

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, thermal parameters, and observed and calculated structure factor amplitudes and a fully numbered ORTEP plot (6 pages). Ordering information is given on any current masthead page.

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(15) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 706–708.

(16) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440–4451.

(17) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971; Chapter 7.

Book Reviews

Dictionary of Chemistry and Chemical Technology. By H. Gross (Technische Universität, Dresden). Elsevier Science Publishers: Amsterdam and New York. 1984. German/English: 633 pp. $105.75. ISBN 0-444-99617-6. English/German: 717 pp. $105.75. ISBN 0-444-9418-4.

This is an unusually satisfying dictionary for its thoroughness and clarity. Most users of language-to-language dictionaries have been frustrated by the hordes of obvious or totally obscure terms but the absence of the terms they were actually looking for. This dictionary is an exception, in that the right words are there. it is also distinguished from the horde by the precision of its definitions, in which, for example, chemical formulas are often given in addition to names ("chromate red" is not only translated as "chromrot", "chromzinnober", or "Persischrot", but the formula $Pb(OH)_2{\cdot}PbCrO_4$ is added). Synonyms and alternatives are given in abundance. the temptation to make literal translations, which are befuddling, has been stoutly resisted; "squirrel-cage disintegration", for example, is translated as "Schlagkorbmühle". The dictionary is also up to date, and antiquated terms are few, whereas terms of modern origin, such as "reprography", are well represented. There are, of course, some arcane entries, such as "Maul: inlet (of a jaw breaker)", but probably those with a need to look up such terms will understand what is meant.

Finally, it should be noted, the print is easily readable, unlike that in some dictionaries in which the publishers have tried to put too much on too few pages.

Treatise on Heavy Ion Science. Volume 6. Astrophysics, Chemistry and Condensed Matter. Volume 7. Instrumentation and Techniques. Volume 6: Edited by D. Allen Bromley (Yale University). Plenum Press: New York, 1985. xxii + 428 pp. $69.50. ISBN 0-306-41786-3. Volume 7: Edited by D. Allen Bromley (Yale University). Plenum Press: New York, 1985. xxi + 471 pp. $69.50. ISBN 0-306-41787-1.

Both of these volumes have the same preface. In fact this is the general preface for the entire series. In it the editor states that the field of heavy-ion science now requires an overview of the accomplishments and some "enlightened speculation" about what comes next. The volumes are aimed at workers in the field as well as those involved in neighboring fields—students and professional scientists. There is also the expressed hope that the volumes will be informative to a wider audience in other sciences and technologies. In order to accomplish the stated objectives the editor has enlisted the aid of internationally recognized authorities to write about their own areas of expertise and to write in a way that provides background for students and nonspecialists. He makes no claims for the completeness of the volume.

Volume 6 has 16 contributers. As is so often characteristic of such volumes the style of the contributions is varied and so is the amount of expertise required from the reader. Some of the pieces are tutorial and others written for people with some experience and prior exposure. The topics cover the following subjects: Heavy-ions Reactions in Nuclear Astrophysics, Heavy-Ions in Hot Atom Chemistry, The Stopping and Range of Ions in Matter, Ion Implantation, Heavy-Ion Channeling, The Electronic Polarization Induced in Solids Traversed by Fast Ions, Erosion of Surfaces by Fast Heavy-Ions, Heavy-Ion Damage in Solids, Analysis with Heavy-Ions, and Heavy-Ion Induced Fusion Power.

For the more expert reader many of the chapters represent a current review with a large number of references and for individuals from other disciplines some of the chapters are a useful introduction to the field of heavy-ions.

The impression that I formed about Volume 6 in this series was of a series or collection of essays about heavy-ions. The subject matter of Volume 7 on the other hand lends itself better to a systematic development. It concentrates on problems and techniques that are specific to heavy-ion studies. There are sections on the state of the art in the production of both positive and negative heavy-ions, the preparation of stripping foils for heavy-ion beams, and the preparation of heavy-ion targets. There are additionally sections on analytical instrumentation for the detection and measurement of heavy-ions. Many of the chapters are detailed, featuring useful drawings and schematics. This is a useful volume and again a source for references.

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Photophysics and Photochemistry in the Vacuum Ultraviolet. Edited by S. P. McGlynn (Louisiana State University), G. L. Findley (New York University), and R. H. Huebner (Argonne National Laboratory). D. Reidel Publishing Company: Dordrecht, Holland. 1985. xvi + 960 pp. $99.00. ISBN 90-277-1882-2.

This is the proceedings of a NATO Advanced Study Institute held in Lake Geneva, Wisconsin, in August 1982. It includes 28 papers by chemists and physicists on spectroscopy and photochemistry in the vacuum ultraviolet (VUV), i.e., states with six to several hundred electron volts in energy. The editors's aim has been "to construct a book which is pedagogically useful..., but which still serves as an introduction to state-of-the-art research on highly excited states of atoms and molecules." Indeed, the book is well-organized and a number of the individual papers were written with the contributions of other authors clearly in mind.

Rydberg states dominate many of the discussions, both in experimental and theoretical papers. These states whose energies form a hydrogenic series converging to an ionization potential of the molecule or atom are typically the sharpest states in VUV spectra. Their weak coupling to valence states makes them especially important intermediates in multiphoton photochemistry and ionization. Three tutorial papers by Rau, Lu, and Greene build up the quantum defect theory appropriate to a theoretical description of Rydbergs. It is a rare experimental paper that does not at least mention the states.

Two experimental developments have sharply increased interest in VUV spectroscopy. Synchrotron radiation is now available to investigators willing to travel. Synchrotrons provide a high brightness source of pulsed, polarized photons useful in a variety of absorption, reflection, and ionization spectroscopies. Lasers are also important. While several examples of direct laser emission in the VUV exist, high-resolution spectroscopy usually involves either the use of nonlinear processes to shift tunable visible lasers into the VUV or of nonlinear absorption by molecules themselves as in multiphoton ionization.

Beyond those topics already mentioned are included electron impact spectroscopy, negative-ion states, superexcited states, van der Waals dimers, excitons in rare gas solids, and electric and magnetic field effects, especially magnetic circular dichroism. In addition to purely spectro-

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*Unsigned book reviews are by the Book Review Editor.