a single sharp peak to be observed intermediate between the two resonances, the exchange rate must be on the order of 10 times this value or about $10^5$ Hz. This exchange rate is fast compared with the inverse width of the soft pulse, but must be slow relative to the frequency of the NMR experiment ($10^8$ Hz). Hence, the exchange frequency of protons on the bimetallic catalyst must be from about $10^5$ to $10^7$ Hz.

In summary, we have observed that hydrogen will dissociatively adsorb on Cu–Ru/$SiO_2$ catalysts and populate sites on both Cu and Ru. This direct evidence for hydrogen spillover from Ru onto Cu suggests that hydrogen chemisorption cannot be used to titrate the number of surface Ru atoms in a Cu–Ru bimetallic catalyst.

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## Facile Net Loss of a Carbon Atom from a Constrained Intermediate

Supanna Tivakornpannarai and Edward E. Waali*

*Department of Chemistry, University of Montana*
*Missoula, Montana 59812*

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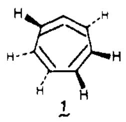
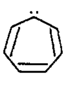
In a study of physically constrained cycloheptatrienylidenes and cycloheptatetraenes, an anthraceno bridged intermediate has been generated and an unusual reaction resulting in the net loss of a lone *carbon atom* has been discovered.

The relationship between cycloheptatetraene (**1**) and cycloheptatrienylidene (**2**) has been the focus of considerable experimental and theoretical effort.[1-4] It now appears that all of the



1



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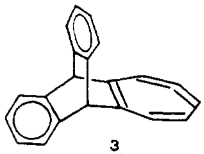

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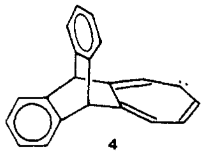


4

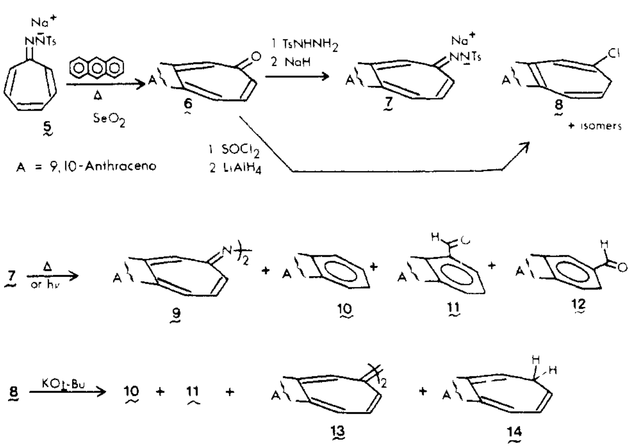
chemistry once attributed to the singlet state of planar **2**[5] should instead be explained in terms of the nonplanar allene **1**.[2-4] Our calculations using both reaction coordinates and vibrational force constants led to the conclusion that planar singlet **2** is a *transition state* for the interconversion of chiral **1** and its enantiomer.[4d]

The tropone **6** has been prepared.[7] The structure of **6** was indicated by high-field NMR spectroscopy and a high-resolution mass spectroscopy and was verified by X-ray crystallographic structure determination. The ketone **6** was converted to **7** and **8** by known methods.[1a] The decomposition of **7** or the reaction of **8** with strong base should give the allene **3** since this type of constraint (C4–C5 bridging using the numbering of **1**) should only reinforce its stability relative to **4**. Upon thermolysis or photolysis, **7** gave the azine **9** and triptycene (**10**) (Table I). In some experiments, the aldehydes **11** and **12**, the dimer **13**, and the cycloheptatriene **14** were also observed.[7]

Table I. Product Yields from the Decomposition of **7** and **8**

| starting material | conditions[b] | yields,[a] % | | | |
|---|---|---|---|---|---|
| | | **9** | **10** | **11** | other |
| **7** | $h\nu$, 30 °C, 0.0212 M, THF | 30 | 5 | | |
| **7** | $h\nu$, 30 °C, 0.0124 M, THF | 9 | 37 | | |
| **7** | Δ, 125 °C, 0.0405 M, diglyme | 32 | 2 | | |
| **7** | Δ, 125 °C, 0.0117 M, diglyme | 18 | 19 | 5 | |
| **7** | Δ, 125 °C, 0.0124 M, $Me_2SO$ | 22 | 12 | | 2 ($Me_2S$) |
| **8** | KO-*t*-Bu, RT,[d] 0.161 M, THF | | 12 | | 45 (13)[c] |
| **8** | KO-*t*-Bu, RT,[d] 0.085 M, THF | | 12 | | 4 (13) |

[a] Isolated yields after preparative thin-layer chromatography (TLC). The remaining material would not move under the TLC conditions. [b] Nitrogen atmosphere. [c] The dimer 13 was not stable to TLC. This represents a column chromatographic purification. It was probably also formed in the previous reactions but was destroyed under the TLC conditions. [d] RT = room temperature.



Although the formations of **11–14** are in some respects unusual under these conditions, they will be discussed at a later time.[8,9]

The formation of **10** requires the net loss of a carbon atom and is, to our knowledge, unknown in carbene or allene chemistry under such mild conditions in solution. The amounts of **9** and **10** are concentration dependent with more **10** being formed at lower concentrations of **7** and **8**.[10] The loss of carbon atoms from quadricyclanylidene (**15**),[11] norbornadienylidene (**16**),[12] and other strained cyclic carbenes[13] has been observed under the much more vigorous conditions of the vacuum pyrolysis of the tosylhydrazone salts at 250–400 °C. The reverse of this type of reaction (benzene + arc-produced carbon atoms giving, ultimately, heptafulvalene) has been reported.[13,14] Thus, the loss of a carbon atom in rea-

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(1) (a) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391. (b) Christensen, L. W.; Waali, E. E.; Jones, W. M. *Ibid.* **1972**, *94*, 2118. (c) Waali, E. E.; Jones, W. M. *Ibid.* **1973**, *95*, 8114. (d) Waali, E. E.; Jones, W. M. *Synthetic Commum.* **1973**, *3*, 49. (e) Waali, E. E.; Jones, W. M. *J. Org. Chem.* **1973**, *38*, 2573. (f) Duell, B. L.; Jones, W. M. *J. Org. Chem.* **1978**, *43*, 4901. (g) Mayor, C.; Jones, W. M. *Tetrahedron Lett.* **1977**, 3855. (h) Reiffen, M.; Hoffmann, R. W. *Ibid.* **1978**, 1107.

(2) Harris, J. W.; Jones, W. M. *J. Am. Chem. Soc.* **1982**, *104*, 7329.

(3) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *Ibid.* **1982**, *104*, 1779.

(4) (a) Tyner, R. L.; Jones, W. M.; Ohrn, Y.; Sabin, J. R. *J. Am. Cvhem. Soc.* **1974**, *96*, 3765. (b) Radom, L.; Schaefer, H. F.; III; Vincent, M. A. *Nouv. J. Chim.* **1980**, *4*, 411. (c) Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*, 6719. (d) Kassaee, M. Z.; Nimlos, M. R.; Downie, K. E.; Waali, E. E. *Tetrahedron* **1985**, *41*, 1579.

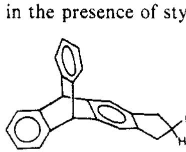
(5) There have been two very recent reports of the matrix isolation ESR spectrum of triplet **2**. (a) Kuzaj, M.; Luerssen, H.; Wentrup, C., private communication from C. Wentrup, 1985. (b) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1986**, *108*, 1713.

(6) Saito, K.; Omura, Y.; Mukai, T. *Tetrahedron Lett.* **1980**, 349.

(7) New compounds (**6–9** and **11–14**) were identified on the basis of their 270-MHz proton NMR spectra, 22.5-MHz carbon NMR spectra, and their high-resolution mass spectra (or satisfactory elemental analysis). Authentic samples of **10–12** were prepared and compared to the materials isolated in the described reactions.

(8) Rearrangements of the type which ultimately give **11** and **12** are discussed in: (a) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353. (b) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479.

(9) The generation of **3** in the presence of styrene gave a 17% yield of *i*



i

in addition to the above products. Such an addition and rearrangement has also been observed from **1**.[1c]

(10) Shevlin, P. B.; Wolf, A. P. *Tetrahedron Lett.* **1970**, 3987.

(11) Brown, W. T.; Jones, W. M. *J. Org. Chem.* **1970**, *44*, 3090.

(12) (a) Moss, R. A.; Dolling, U.-H.; Whittle, J. R. *Tetrahedron Lett.* **1971**, 931. (b) Okumura, K.; Murahashi, S.-I. *Ibid.* **1977**, 3281.

(13) Biesida, K. A.; Kooch, C. T.; Shevlin, P. B. *J. Am. Chem. Soc.* **1980**, *102*, 2098.

(14) The loss of carbon has been observed in the oxidation of tropylium ions (Volpin, M. E.; Kursanov, D. N.; Dulova, V. G. *Tetrahedron* **1960**, *8*, 33), but this is probably not related to the reaction described in the present work.

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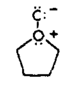
sonably decent yield from **7** or **8** is surprising.

It is highly unlikely that the net elimination of a carbon atom from most strained allenes or carbenes in solution results in a *free* carbon atom. Such processes would be highly endothermic as seen by the following rough estimates for singlet states in the gas phase:[15] $CH_2 \rightarrow$ C atom + $H_2$, $\Delta H = +93$ kcal/mol; **1** → C atom + benzene, $\Delta H = +130$ kcal/mol; **15** → C atom + benzene, $\Delta H = +36$ kcal/mol; **16** → C atom + benzene, $\Delta H = +58$ kcal/mol. The conclusion would not be grossly different for the triplet states. Ring strain would raise the energy of the starting material and would lower the $\Delta H$ of reaction. In fact, black deposits were observed from **15** when it was generated in the vapor phase.[11]

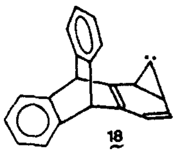
In solution, it is much more likely that the carbon atom is transferred to a nucleophilic atom or bond in the solvent. It was reported that 15 reacts with THF to give CO and ethylene.[11] In the thermolysis or photolysis of **7**, the infrared spectra of the evolved gases showed CO (bands centered at 2110 and 2170 $cm^{-1}$) and ethylene (bands centered at 3110 and 3035 $cm^{-1}$).[18] Our MNDO calculations indicate the direct transfer of the carbon atom to the oxygen atom of THF (producing **17**) would lower the above $\Delta H$ values by about 25 kcal/mol.

The thermolysis of **7** in $Me_2SO$ gave **10** and $Me_2S$. Deoxygenation of $Me_2SO$ by carbenes has also been reported to give ketones,[18] but the ketone **6** was not observed in the present work.

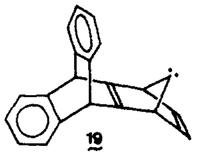
We can only speculate on the identity of the intermediate which gives up the carbon atom. 1-Triptycylmethylene and 2-triptycylmethylene, which are related to **3** by carbene–allene rearrangements,[8] were shown not to be involved since their separate generation from their tosylhydrazone salts gave a large number of normal products but no **10**.[19] Rearrangement of **3** to the norcaradienylidene **18** or the norbornadienylidene **19** might be followed by the loss of a carbon atom. A recent report has considered the involvement of norcaradienylidenes and norbornadienylidenes in rearrangements.[8b] The formation of **14** by hydrogen abstraction might implicate the triplet version of **4** in some of these reactions. Work concerned with these intermediates and designed to test for the necessity of a through-space interaction with the benzo rings is in progress.



**17**



**18**



**19**

**Acknowledgment.** This work was supported by the Monts-NSF project ISP-8011449, a Murdock Charitable Trust Grant of Research Corporation, and donors of the Petroleum Research Fund, administered by the American Chemical Society. University of Montana Faculty Research Grants were also used in this research. MONTS funds were also used in the purchase of the 270-MHz NMR spectrometer used in this work. A 360-MHz proton NMR spectrum was also obtained at the Colorado State University Regional NMR Center (NSF CHE-8208821). The assistance of Dr. P. W. Jennings, Dr. K. Emerson, L. J. Sears, and R. Larsen (Montana State University) in obtaining high-resolution mass spectrometric and X-ray crystallographic information is sincerely appreciated.

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(15) The heats of formation used in these estimates came from Waali (Waali, E. E., unpublished singlet MNO results), for $CH_2$ (107 kcasl/mol), **15** (186 kcal/mol), **16** (163 kcal/mol), and **17** (119 kcal/mol); Ref. 4d for **1** (91 kcal/mol); Dewar and Thiel (Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, **99**, 4970) for benzene (21.2 kcal/mol); and *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2, 83 for the singlet carbon atom (200 kcal/mol).

(16) Skell, P. S.; Plonka, J. H.; Engel, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 6179.

(17) Oda, R.; Mieno, M.; Hayashi, Y. *Tetrahedron Lett.* **1967**, 2363.

(18) Birge, R. R.; Haney, J. L.; Ricco, E. "Vapor Phase Spectra for Air Pollution Studies"; Report AFCEC-TR-75-15, Air Force Civil Engineering Center, Tyndall AFB, FL, 1975.

(19) Pang, D.; Tivakornpannarai, S., University of Montana, unpublished results.

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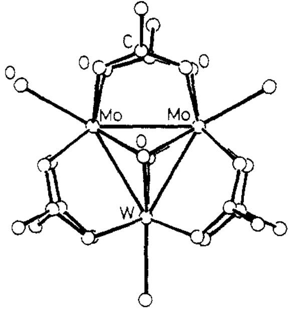
## Molybdenum–Tungsten Mixed-Metal Trinuclear Clusters, $[Mo_2W(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ and $[MoW_2(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$

Bateer Wang,[1] Yoichi Sasaki,* Akira Nagasawa, and Tasuku Ito

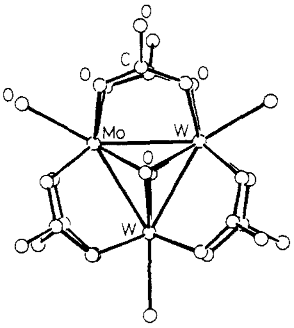
*Department of Chemistry, Faculty of Science*
*Tohoku University, Aoba, Aramaki, Sendai 980, Japan*

*Received June 10, 1986*

A number of metal–metal bonded mixed-metal compounds are known for carbonyl clusters[2] but only a few for noncarbonyl clusters with no strong σ-donor and π-acceptor ligand.[3] The latter clusters would show a more fundamental aspect of the metal–metal bond, since the metal ions in carbonyl clusters are electronically perturbed by carbonyl ligands. We wish to report here two new mixed molybdenum(IV)–tungsten(IV) trinuclear clusters, orange red $[Mo_2W(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ (abbreviated as $Mo_2W$) and orange $[MoW_2(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ ($MoW_2$). Since the corresponding red trimolybdenum(IV)[4] ($Mo_3$) and yellow tritungsten(IV)[5] ($W_3$) clusters are known,[6] a whole series of four complexes, $Mo_3$, $Mo_2W$, $MoW_2$, and $W_3$, are now available. To our knowledge, this is the first complete series of trinuclear metal–metal bonded non-carbonyl clusters involving two metal ions.[7,8]



$Mo_2W$



$MoW_2$

Sodium tungstate dihydrate (5 g; 0.015 mol) and 10 g of zinc dust in 300-$cm^3$ acetic anhydride was refluxed for 15 min. After addition of 5 g (0.021 mol) of sodium molybdate dihydrate and 10 g of zinc dust the reflux was continued for further 24 h. The precipitate (ca. 18 g) was dissolved in 1 $dm^3$ of 0.4 M HBr and

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(1) On leave from Department of Chemistry, Inner Mongolia Pedagogical University, Huhhot, People's Republic of China.

(2) See: Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 4th ed.; Wiley: New York, 1980; pp 1062, 1094. Also, for recent examples: (a) Rhodes, L. F.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 1759–1760. (b) Bogan, L. E., Jr.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 3843–3850. (c) Arndt, L. W.; Darensbourg, M. Y.; Fackler, J. P., Jr.; Lusk, R. J.; Marler, D. O.; Youngdahl, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 7218–7219. (d) Doyle, G.; Eriksen, K. A.; Van Engen, D. *J. Am. Chem. Soc.* **1985**, *107*, 7914–7920.

(3) Some examples. (a) $[CrMoCl_9]^{3-}$: Matson, M. S.; Wentworth, R. A. D. *J. Am. Chem. Soc.* **1974**, *96*, 7837–7839. (b) $MoW((CH_3)_3CCOO)_4$: Katovic, V.; Templeton, J. L.; Hoxmeier, R. J.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 5300–5302. Katovic, V.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 5586–5587. (c) $CrMo(CH_3COO)_4$: Garner, C. D.; Senior, R. G.; King, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 3526–3529.

(4) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243–244. Birnbaum, A.; Cotton, F. A.; Dori, Z.; Marler, D. O.; Reisner, G. M.; Schwotzer, W.; Shaia, M. *Inorg. Chem.* **1983**, *22*, 2723–2726 and references cited therein.

(5) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Kuppers, H.; Miller, M.; Sektowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245–3253.

(6) Cotton, F. A. *Polyhedron* **1986**, *5*, 3–14.

(7) Whole series of $[M_2M'(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(H_2O)_3]^+$ is known for iron(III)–chromium(III), in which the metal–metal bond is absent (Catterick, J.; Thornton, P. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291–362). See also: Straughan, B. P.; Lam, O. M. *Inorg. Chim. Acta* **1985**, *98*, 7–10.

(8) Trinuclear mixed-metal molybdenum–tungsten complexes, $Mo_2W(\mu_3\text{-}O)(\mu_3\text{-}O\text{-}i\text{-}Pr)(\mu\text{-}O\text{-}i\text{-}Pr)_6(O\text{-}i\text{-}Pr)_3$ (Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kober, E. M. *Inorg. Chem.* **1985**, *24*, 241–245) and $Mo_2W(\mu_3\text{-}CCH_3)(\mu_3\text{-}O\text{-}i\text{-}Pr)(\mu\text{-}O\text{-}i\text{-}Pr)_6(O\text{-}i\text{-}Pr)_3$ (Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234–1241), were reported, but their $MoW_2$ counterparts were only poorly characterized or not known.

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