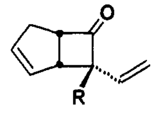
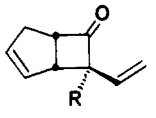
7672 J. Am. Chem. Soc. **1982**, *104*, 7672-7673

20 h) afforded in each case the expected bicyclo[4.2.2]decadienone as major product. Unfortunately, annulation employing the less stable and ketenophilic dienes isoprene and (E)-1,3-pentadiene proved unsuccessful. No reaction was detected at 80–120 °C in these cases, and at higher temperatures dimerization of the conjugated dienes intervened.

An alternative version of the [4 + 4] annulation involves generation of the intermediate vinylketenes by the triethylamine-promoted 1,4-dehydrochlorination of α,β-unsaturated acid chlorides.[13] In some cases it is possible to effect ketene generation, [2 + 2] cycloaddition, and [3,3] sigmatropic rearrangement in a single step, while other annulations are best accomplished via the isolation and purification of the intermediate 2,3-divinylcyclobutanone derivatives. Thus, heating the vinylketene–cyclopentadiene cycloadduct **15**[8] in benzene at 120 °C for 18 h furnished bicyclo[4.2.1]nona-3,7-dien-2-one (**9**) in 55% yield. The identity of this annulation product was established unambiguously by its conversion to bicyclo[4.2.1]nonan-2-one[14] upon hydrogenation (10% Pd–C, CH_3OH, 25 °C, 4.5 h).

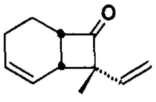


15, R = H
17, R = CH_3



16, R = H
18, R = CH_3

Similarly, rearrangement of the mixture of stereoisomeric cycloadducts **17** and **18** (30:70) obtained from the reaction of methylvinylketene with cyclopentadiene[7b,c,8] proceeded smoothly in toluene (160 °C, 19 h) to afford the annulation product **10** in 53% yield.[15] Both the endo- and exo-vinyl isomers in this and related systems are amenable to rearrangement. Reaction of methylvinylketene with 1,3-cyclohexadiene as described previously[8] furnished pure samples of the stereoisomeric cycloadducts **19** and **20**. Separate thermolysis of these compounds then led in each case to the formation of bicyclodecadienone **11**.[16] For preparative purposes the mixture of **19** and **20** (27:73) was converted to **11** (toluene, 160 °C, 19 h, 55% yield) without prior separation of isomers.



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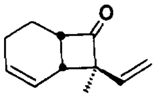
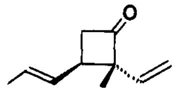


20



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The dehydrochlorination version of the [4 + 4] annulation has been successfully applied to less ketenophilic and less stable conjugated dienes such as (E)-1,3-pentadiene and 1-vinylcyclopentene. As expected, [2 + 2] cycloaddition of methylvinylketene in these cases occurs exclusively at the less substituted double bond of the diene, resulting in the eventual formation of a single annulation product regioisomer. However, [4 + 4] annulation employing the more sterically hindered diene 3-methylenecyclohexene proved unsuccessful under a variety of conditions. Finally, [4 + 4] annulation was also accomplished by employing chlorovinylketene, which was generated by the dehydrochlorination of (Z)-2-chloro-2-butenoyl chloride.[7k,17]

Although in some cases the annulation proceeds in disappointing overall yield, it should be recognized that a series of three discrete reactions constitutes the total process. Furthermore, we anticipate that this [4 + 4] annulation will proceed with high stereoselectivity, as a consequence of the stereospecific nature of each of the pericyclic reactions that comprise the overall method. Further studies are underway in our laboratory to confirm this prediction, to develop more efficient versions of the annulation, and to demonstrate its utility in the synthesis of natural products.

Acknowledgment. We thank the National Institutes of Health and Eli Lilly and Co. for generous financial support.

Supplementary Material Available: Spectroscopic data for all new compounds (6 pages). Ordering information is given on any current masthead page.

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[12] Isolated yields of purified products. Annulation product **13** could only be obtained in ca. 80% purity; **8** could only be obtained in ca. 90% purity in multigram large-scale runs but could be obtained pure in smaller scale runs. Infrared, 250-MHz ^1H NMR, ^{13}C NMR, and high-resolution mass spectral data were fully consistent with the assigned structures (see supplementary material).

[13] See ref 7a–c,e,h,i,k, 8 and the following; (a) Ozeki, T.; Kusaka, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2686. (b) Iwakura, Y.; Toda, F.; Iwata, R.; Torii, Y. *Ibid.* **1969**, *42*, 841. (c) Wuest, J. D.; Madonik, A. M.; Gordon, D. C. *J. Org. Chem.* **1977**, *42*, 2111. (d) Danheiser, R. L.; Sard, H. *Ibid.* **1980**, *45*, 4810. (e) Mohmand, S.; Hirabayashi, T.; Bock, H. *Chem. Ber.* **1981**, *114*, 2609.

[14] Mp 90–93.5 °C, semicarbazone mp 204–205 °C; (lit. mp 92–93 °C, semicarbazone mp 206 °C: Sadlo, H.; Kraus, W. *Tetrahedron* **1978**, *34*, 1965.

[15] Subsequent to the completion of this investigation, a report appeared by Dreiding and co-workers describing the preparation of **10** (and several related bicyclo[4.2.1]nonadienones) by an identical route; see ref 7k.

[16] The transformation of the exo-vinyl isomer **20** to **11** most likely proceeds via the diradical-mediated epimerization[3e] of **20** to **19**.

[17] Prepared in 50% overall yield from crotonic acid via treatment with (a) Cl_2 in CS_2 25 °C for 6 h, (b) pyridine at 115 °C for 3 h, and finally (c) $SOCl_2$, 90 °C, 1.5 h.

Stabilization of Dimercury through Coordination to Platinum Cluster Units

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Although the chemistry of Hg_2^{2+} has been extensively studied, we are unaware of reports relating to the existence of the Hg_2 moiety in a molecular compound. In the course of our studies on tri- and tetranuclear platinum clusters[1,2] we observed that they reacted with metallic mercury giving deep blue-green or blue solutions from which mixed platinum-mercury clusters were isolated.

Thus, reaction of a solution of $[Pt_3(\mu_2\text{-}CO)_3(PPh\text{-}i\text{-}Pr_2)_3]$, **1**,[1] with metallic mercury gave a blue-green solution from which dark violet crystals of $[Pt_3Hg(CO)_3(PPh\text{-}i\text{-}Pr_2)_3]_2$, **2**, could be obtained.

The X-ray structure of **2** was determined.[3] The molecule, shown schematically in Figure 1, consists of *two* triangular $\{Pt_3(\mu_2\text{-}CO)_3(PPh\text{-}i\text{-}Pr_2)_3\}$ units *each capped by a mercury atom*, these two units being joined through the mercury atoms, which

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[1] Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chim. Acta* **1981**, *48*, 153.

[2] Moor, A.; Pregosin, P. S.; Venanzi, L. M. *Inorg. Chim. Acta* **1982**, *61*, 135.

[3] Crystals of **2** were obtained from acetone and are air stable. A crystal of approximate dimensions 0.25 × 0.30 × 0.20 mm was chosen for the data collection. Compound **2** ($[C_{78}H_{114}Hg_2Pt_6P_6O_6]$, , M_r 2905.34) crystallizes in the triclinic space group $P\bar{1}$, with a = 12.162 (3) Å, b = 13.712 (2) Å, c = 14.730 (4) Å, α = 93.30 (2)°, β = 93.82 (2), γ = 96.59 (1)° (least-squares-refined values obtained from 23 high-angle reflections measured on an automatic diffractometer), $Z = 2$, V = 2429.5 (4) Å^3, ρ_c = 2.026 g cm^{-3}. Data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature up to $2\theta_{max} \leq 50.0°$ (Mo K$\bar{\alpha}$ graphite monochromated radiation) with an $\omega/2\theta$ scan. The scan speed was kept constant (4° min^{-1}) with a variable scan width (according to $\theta = 0.90 + 0.35 \tan \theta$); background was measured at each side of the peaks for half the time of the scan. A total of 8560 independent reflections were collected, of which 6588 were considered as observed (having $I_{net} \geq 3\sigma(I)$) and subsequently used. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares analysis with use of anisotropic thermal factors for the Hg, Pt, and P atoms and isotropic for the others; a correction for the real part of the anomalous dispersion has been allowed for. Scattering factors were taken from the "International Tables for X-ray Crystallography", Vol. IV. The present conventional agreement factor is 0.076 (for the observed reflections).

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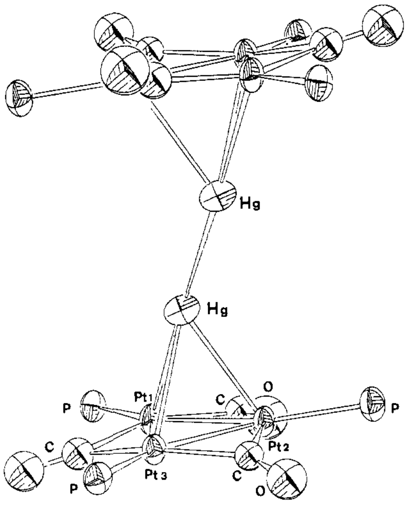

Figure 1. ORTEP drawing of the molecule $[Pt_3Hg(\mu_2\text{-}CO)_3(PPh\text{-}i\text{-}Pr_2)_3]_2$. Carbon atoms of the phosphine ligands have been omitted for clarity. Some relevant bond lengths (Å) and angles ° are as follows (av–average value; the ± sign where given refers to the mean-square deviation from the mean): Hg···Hg′, 3.225 (1); Hg–Pt(1), 2.968 (1); Hg–Pt(2), 2.931 (1); Hg–Pt(3), 3.084 (1); Pt(1)–Pt(2), 2.661 (1); Pt(1)–Pt(3), 2.651 (1); Pt(2)–Pt(3), 2.662 (1); Pt–P(av), 2.257 ± 0.15 (5); Pt–C(av), 2.05 ± 0.03 (2); P–C(av), 1.83 ± 0.03 (2); C–O(av), 1.20 ± 0.005 (3); Pt(1)–Hg–Pt(3), 51.92 (2); Pt(1)–Hg–Pt(2), 53.63 (2); Pt(2)–Hg–Pt(3), 52.46 (2); Pt(1)–Pt(2)–Pt(3), 59.74 (2); Pt(1)–Pt(3)–Pt(2), 60.12 (2); Pt(2)–Pt(1)–Pt(3), 60.14 (2).

are at a distance of 3.225 (1) Å. It is noteworthy that in metallic mercury the crystalline α form has each Hg atom surrounded by six nearest neighbors at 2.99 Å and another six at 3.47 Å. It should also be noted that the Hg–Hg distances in the Hg_2X_2 salts for X = halide are 2.49–2.51 Å.[4] The two halves of the molecule are related through a center of symmetry, and thus, the two Pt_3 units are staggered. Each mercury atom lies above a Pt_3 triangle, with nonequivalent Pt–Hg distances ranging from 2.932 to 3.084 (1) Å. The bond distances within the Pt_3 triangles are nonequivalent and slightly longer than those found for $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_3]$, **3** (2.655 ± 0.002 Å, average value), and comparable with the basal Pt–Pt separation in $[Pt_3(\mu_2\text{-}CO)_3(PCy_3)_4]$, **4** (2.675 (1) Å.[6] The carbonyl ligands are symmetrically bridging and are bent away from the mercury atoms (mean deviation of the oxygen atoms from the least-squares planes defined by the Pt_3 triangles: 0.54 Å).

Compounds $[Pt_3Hg(\mu_2\text{-}CO)_3(P\text{-}i\text{-}Pr_3)_3]_2$, **5**, and $[Pt_3Hg(\mu_2\text{-}CO)_3(PEt_2\text{-}t\text{-}Bu)_3]_2$, **6**, were also prepared as described for **2**.

^{31}P, ^{195}Pt, and ^{199}Hg NMR studies show that, in toluene solution, the mixed-metal clusters are still fluxional down to ca. −90 °C. The ^{31}P and ^{195}Pt NMR spectra, however, are very similar to those found for the parent Pt_3 cluster **1**, suggesting that the fluxional process is associated with the mercury atoms.

The solid-state structure of **2** indicates that there is a weak Hg–Hg interaction. The bonding between this unit and the Pt_3 fragments can be described, to a first approximation, by a linear combination of (1) one empty σ-type orbital of one of the coordinatively unsaturated Pt_3 fragments, (2) the filled 6s orbital of one mercury atom, (3) the 6s orbital of the other mercury atom, and (4) the empty σ-type orbital of the second Pt_3 fragment. This gives rise to one strongly bonding and one weakly bonding molecular orbital that accommodate the four bonding electrons. The weak Hg–Hg interaction arises from the nonbonding character between these two atoms of the HOMO.

It is noteworthy that the reaction of $[Pt_4(\mu_2\text{-}CO)_5(PEt_3)_4]$ with metallic mercury[7] gives a compound of the composition $\{Hg[Pt_3(\mu_2\text{-}CO)_3(PEt_3)_3]_2\}$, **7**, which could be similar to $\{Hg[Pt_3(\mu_2\text{-}2,6\text{-}Me_2C_6H_3NC)_3(2,6\text{-}Me_2C_6H_3NC)_3]_2\}$,[8] in which a single mercury atom is sandwiched between the two Pt_3 triangles.

Acknowledgment. A.M., P.S.P., and L.M.V. gratefully acknowledge financial support from the Swiss National Science Foundation.

Registry No. 1, 77760-50-0; **2**, 83803-81-4; **5**, 83781-26-4; **6**, 83781-27-5; **7**, 83801-82-5; Hg, 7439-97-6; Pt, 7440-06-4; $[Pt_4(\mu_2\text{-}CO)_5(PEt_3)_4]$, 83781-28-6.

Supplementary Material Available: Final positional and thermal parameters for **2** (Table I) and anisotropic temperature factors for **2** (Table II) (3 pages). Ordering information is given on any current masthead page.

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(5) Albinati, A. *Inorg. Chim. Acta* **1977**, *22*, L31.

(6) Albinati, A.; Carturan, G.; Musco, A. *Inorg. Chim. Acta* **1976**, *16*, L3.

(7) Moor, A.; Venanzi, L. M., unpublished results.

(8) Yamamoto, Y.; Yamazaki, H.; Sakurai, T. *J. Am. Chem. Soc.* **1982**, *104*, 2329.

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*Book Reviews**

Organic Electronic Spectral Data. Volume XVII. Edited by J. P. Phillips, D. Bates, H. Fever, and B. S. Thyagarajan. John Wiley & Sons, New York. 1981. xiii + 1060 pp. $100.00.

With this volume, nearly 400 000 UV–vis spectra have been recorded in this series, which began in 1956. It now appears annually; this volume includes data from the literature published in 1975. The data given consist of the wavelength maxima with the corresponding extinction coefficients, the solvent in which the spectrum was measured, and the reference to the original source. The material is arranged in tabular form in formula-index order; the specific compound is identified by its name in Chemical Abstracts style.

100 Jahre Beilstein: 1881–1981. Beilstein Institut, Varrentrappstrasse 40–42, D-6000 Frankfurt 90, FRG. 1981. 128 pp. Gratis.

This charming *Festschrift* may be obtained free of charge, so long as a small supply lasts, by writing to the Institut. It is a valuable contribution to the history of chemistry and contains photographs of notables in the development of "Beilsteins Handbuch der Organischen Chemie", beginning with Friedrich Konrad Beilstein. He began compiling, as early as 1860, the data for what was to become the Handbuch. That edition, which appeared in the period 1880–1883, contained only about 15 000 compounds. The Handbuch soon outgrew the abilities of a single editor, and as organic chemistry has burgeoned, the preparation of "Beilstein" has passed successively to a pair of editors, an editorial team, and finally to the Beilstein Institut, a foundation with its own large building and staff of about 150 full-time professionals.

The content of "Beilstein" has also evolved with its subject, although its guiding principle has endured: to list every known organic compound, with a concise but critically examined summary of the physical and chemical properties of each, accompanied by the pertinent references. It remains the only complete source of such information, which is contained in over 240 volumes and 200 000 pages so far. New volumes in the IVth supplement appear at the rate of about 17 per year. Its completion is expected in 1985, and the IVth supplement, which will bring the coverage close to present times, is already in active preparation. It will embody a major change: it will be produced in English.

The value of "Beilstein" as an archive of information is generally known, but its special and unique features are not widely understood and appreciated as they should be. The fact that all the information on one compound can be found in one place has several advantages: it saves one the sometimes great effort and time of assembling the scattered primary

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