

Figure 1. A view of the $[\text{Pt}_3\text{Cl}(\text{HC}\equiv\text{CH})(\text{dppm})_3]^+$ cation. Selected bond lengths are as follows: Pt(1)–P(1), 2.25 (1); Pt(1)–P(6), 2.28 (1); Pt(2)–P(2), 2.27 (1); Pt(2)–P(3), 2.24 (1); Pt(3)–Cl, 2.41 (1); Pt(3)–P(4), 2.33 (1); Pt(3)–P(5), 2.25 (1) Å. For clarity only the ipso carbon atoms of phenyl rings A–L are displayed, and only one of the two orientations of disordered ring J is shown. Probability ellipsoids (50%) are shown.

unique in being supported by only one M–M bond. The C(4)–C(5) bond length [1.40 (4) Å] is normal,⁶ and the Pt(2)–C(4)–C(5) and C(4)–C(5)–Pt(3) angles [119 (2) and 112 (2)°] deviate only slightly from 120° despite the opening of the Pt(2)–C(4)–C(5)–Pt(3) torsion angle to –30 (1)°. The angle between the C(4)–C(5) and Pt(2)–Pt(3) vectors is 17°. The presence of the unsymmetrical μ_3 –(η^2 -||) alkyne in **2**, **4**, and **5** was confirmed by multinuclear NMR studies. For example, **2** gave six ^{31}P resonances and three ^{195}Pt resonances, **2*** (prepared from $\text{H}^{13}\text{C}^{13}\text{CH}$) gave two ^{13}C resonances each of which was a doublet due to $^1\text{J}(\text{CH})$ coupling in the ^1H coupled spectrum, and **2**** (prepared from DCCD) gave two ^2H resonances.¹²

The complexes **3** and **6** contain the μ_3 –(η^2 -⊥) alkyne as shown by NMR analysis.¹³ At low temperature, **3** and **6** each give three ^{31}P and two ^{195}Pt resonances, showing the presence of a plane of symmetry perpendicular to the Pt_3 plane. The ^{13}C NMR of **3*** (prepared from $\text{H}^{13}\text{C}^{13}\text{CH}$) and the ^2H NMR of **3**** (prepared from DCCD) each contained two resonances, thus ruling out a μ_3 –(η^2 -||) structure which would contain only one resonance in each case. The NMR data establish the presence of Pt^1Pt^2 bonds, but no evidence is present for Pt^2Pt^2 bonding.¹³ The complexes **3** and **6a** are fluxional at room temperature, indicating that rotation of the alkyne with respect to the Pt_3 triangle can occur (**3** \rightleftharpoons **3'** \rightleftharpoons **3''**, Scheme I). It is particularly interesting that the bonding mode depends on the electron count of the cluster; there are precedents for the μ_3 –(η^2 -⊥) mode being favored in electron-poor clusters,¹⁴

but we know of no precedent for the easy interconversion with the μ_3 –(η^2 -||) mode shown in Scheme 1.

There are several interesting analogies with surface chemistry. First, it is possible to arrange reagents in order of affinity for the Pt_3 unit, $\text{H}_2\text{S} > \text{HCCH} > \text{CO}$. Thus acetylene will displace CO (**1** \rightarrow **3**) and H_2S will displace both CO from **1** or acetylene from **3** to give $[\text{Pt}_3\text{H}(\mu_3\text{-S})(\mu\text{-dppm})_3]^+$, **7**,¹⁵ but the reverse reactions do not occur. The same series applies to the Pt(111) surface.² One acetylene can displace another reversibly, as in the reaction of excess propyne with **3** to give **6a**.

Next, coordination of acetylene leads to cleavage of Pt–Pt bonds, with there being three such bonds in the 42e complex **1**,⁵ probably two in the 44e complex **3**; and only one Pt–Pt bond in the 46e complexes **2** and **4**.¹⁶ This is an extreme analogy for the weakening of Pt–Pt bonding predicted when acetylene binds to the Pt(111) surface.^{3c} In these model compounds, the alkyne can bind in a μ_3 –(η^2 -||) or μ_3 –(η^2 -⊥) bonding mode, whereas the μ_3 –(η^2 -||) mode is favored on the Pt(111) surface.^{2,3}

Acknowledgment. We thank NSERC (Canada) and SERC (U.K.) for support.

Supplementary Material Available: Details of X-ray analysis and tables of fractional coordinates, anisotropic displacement parameters, and selected bond distances and angles (10 pages); tables of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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(16) We consider that acetylene oxidatively adds to the cluster **1** (i.e., we consider it as $\text{C}_2\text{H}_2^{2+}$). Under these conditions, Pt^1 and Pt^2 are platinum(I) while Pt^3 is square planar platinum(II), though Pt^3 in **4** is tetrahedrally distorted [P–Pt(3)–P, 159 (1)°; C–Pt(3)–Cl, 165 (1)°]. The complex **7** and $[\text{Pd}_3(\text{CN})(\mu_3\text{-S})(\mu\text{-dppm})_3]^+$ can be considered similarly (4e S versus 4e HCCH ligand) but have higher symmetry. However, coordination of Lewis bases does not disrupt Pt–Pt bonds, for example, in the 46e cluster $[\text{Pt}_3(\mu\text{-CO})(\mu\text{-Me}_2\text{PCH}_2\text{PMe}_2)_4]^{2+}$. Ferguson, G.; Lloyd, B. R.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1986**, 25, 4190–4197. Ling, S. S. M.; Hadji-Bagheri, N.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1987**, 26, 231–235.

Interconversion of Bicyclooctadienes and Cyclooctatrienes Formed by Intramolecular Photocycloaddition of Phenyl Ketones Containing Remote Double Bonds

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We recently reported that *o*- and *p*-alkenoxypheyl ketones undergo a rare¹ intramolecular 2 + 2 *ortho* photocycloaddition of the remote double bond to the benzene ring to yield bicyclooctadienes that rearrange thermally to cyclooctatrienes.² We now find that the major stable photoproduct from these reactions is a bicyclo[4.2.0]octa-2,7-diene, which is a secondary photoproduct of the initial 2 + 2 adduct, a bicyclo[4.2.0]octa-2,4-diene. Both bicyclooctadienes rearrange thermally to cyclooctatrienes, the stability of which depends on substitution.

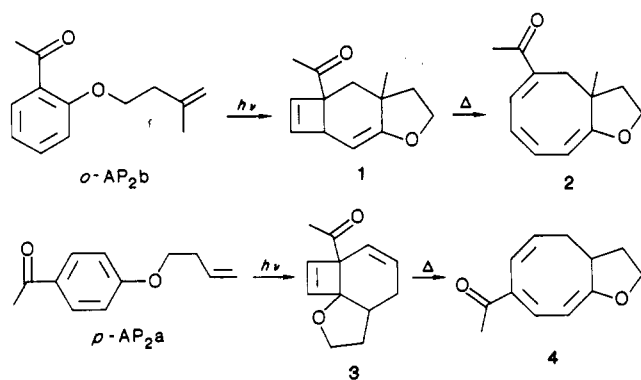
Chart I illustrates the compounds that we have studied. Irradiation (313 or 365 nm) of any of the compounds (except *o*-APd) in a variety of solvents (benzene, acetonitrile, methanol)

(1) (a) Double bond: Sket, B.; Zupancic, N.; Zupan, M. *Tetrahedron* **1986**, 42, 753. (b) Triple bond: Lippke, W.; Ferree, W.; Morrison, H. *J. Am. Chem. Soc.* **1974**, 96, 2134.

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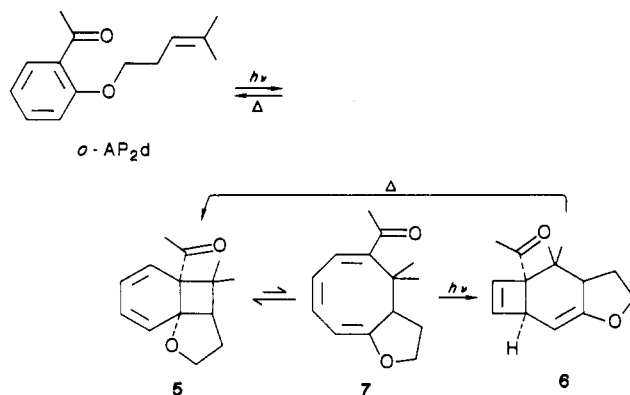
(12) NMR data (refs Me_4Si , H_3PO_4 , K_2PtCl_4) for **2** in CD_2Cl_2 : ^1H δ 11.80 [*m*, $^2\text{J}(\text{Pt}^2\text{H})$ 54, $^3\text{J}(\text{Pt}^3\text{H})$ 66, $^3\text{J}(\text{Pt}^1\text{H})$ 16, $^3\text{J}(\text{HH})$ 8, C^4H], 7.85 [observed in ^2H NMR of **2****, obscured in ^1H , CH^5]; ^{13}C of **2*** 201 [*m*, $^1\text{J}(\text{Pt}^2\text{C})$ 650, $^1\text{J}(\text{CH})$ 152, C^4], 88 [*m*, $^1\text{J}(\text{Pt}^3\text{C})$ 530, $^1\text{J}(\text{CH})$ 163, C^2]; ^{13}C of **2** (^{13}CO) 174 [*s*, $^1\text{J}(\text{PtC})$ 1000, CO]; ^{31}P –12.6 [P^1], –6.6 [P^2], 9.1 [P^3], 10.3 [P^4], 12.1 [P^5], 2.6 [P^6]; ^{195}Pt –3300 [*m*, $^1\text{J}(\text{PtP}^6)$ 3350, $^1\text{J}(\text{PtP}^1)$ 4050, $^1\text{J}(\text{PtP}^2)$ 2100, Pt^1], –2840 [*m*, $^1\text{J}(\text{PtP}^2)$ 2400, $^1\text{J}(\text{PtP}^3)$ 3450, $^1\text{J}(\text{PtP}^4)$ 2100, $^1\text{J}(\text{PtP}^5)$ 900, $^2\text{J}(\text{PtP}^6)$ 600, $^1\text{J}(\text{PtP}^5)$ 170, Pt^2], –2920 [*m*, $^1\text{J}(\text{PtP}^4)$ 2850, $^1\text{J}(\text{PtP}^5)$ 3000, Pt^3]; all PtP and PtC couplings were confirmed by recording both ^{31}P and ^{195}Pt or ^{13}C and ^{195}Pt spectra; IR $\nu(\text{CO})$ 2090 cm^{-1} .

(13) NMR data for **3** in CD_2Cl_2 at –80 °C: ^1H 12.67 [*m*, $^2\text{J}(\text{Pt}^1\text{H})$ 128, $^3\text{J}(\text{Pt}^2\text{H})$ 70, C^1H]; 7.15 [C^2H , obscured in ^1H , confirmed by ^1H – ^1H correlation]; ^{13}C of **3*** 171.1 [*m*, $^1\text{J}(\text{Pt}^1\text{C})$ 440, $^1\text{J}(\text{Pt}^2\text{C})$ ~ 80, $^1\text{J}(\text{CC})$ 40, $^1\text{J}(\text{CH})$ 187, C^1], 73.4 [*m*, $^1\text{J}(\text{Pt}^2\text{C})$ ~ 120, $^1\text{J}(\text{CH})$ 188, C^2]; ^{31}P –9.8 [*m*, $^1\text{J}(\text{PtP}^1)$ 2680, $^3\text{J}(\text{P}^3\text{P}^5)$ 80, P^6], –18.6 [*m*, $^1\text{J}(\text{PtP}^2)$ 3750, P^6], 7.30 [*m*, $^1\text{J}(\text{PtP}^2)$ 4240, $^2\text{J}(\text{PtP}^1)$ 490, P^5]; ^{195}Pt –2278 [*m*, $^1\text{J}(\text{PtP}^1)$ 2010, $^1\text{J}(\text{PtP}^2)$ 440, $^1\text{J}(\text{PtP}^3)$ 2680, Pt^1], –3471 [*m*, $^1\text{J}(\text{PtP}^1)$ 2010, $^1\text{J}(\text{PtP}^3)$ 3750, $^1\text{J}(\text{PtP}^5)$ 4240, Pt^2]. NMR at 20 °C: ^1H 9.91 [*br*, $\text{C}^1\text{H} + \text{C}^2\text{H}$], 5.11 [*m*, $^2\text{J}(\text{HH})$ 13, $^3\text{J}(\text{PtH})$ 76, $\text{P}_2\text{CH}^3\text{H}^3$], 3.56 [*m*, $^2\text{J}(\text{HH})$ 13, $\text{P}_2\text{CH}^3\text{H}^3$]; ^{13}C 122 [*br*, $\text{C}^1 + \text{C}^2$]; ^{31}P –7.3 [*br*, $^1\text{J}(\text{PtP}^1)$ 3580, P^1]. An account of the fluxionality, which is intramolecular, will be given elsewhere.



followed by GC separation (columns $\geq 200^\circ\text{C}$) always provides yellow cyclooctatrienes.³ The GC chemical yields of the products range from 70% to 100%.⁴ Although all of the ketone solutions turned yellow during initial stages of irradiation, they became colorless after complete photoconversion of reactant, as Figure 1 shows for *o*-AP₂b. The transient intermediate formed within 1 min of irradiation has a λ_{max} at 370 nm corresponding to that of the isolated cyclooctatriene. NMR spectra of completely reacted 10^{-2} M solutions indicate quantitative conversion of every acetophenone including *o*-AP₂d to a bicyclo[4.2.0]octa-2,7-diene. For AP₂a and AP₂b, these are the *only* products detectable by FT-NMR even at low and modest conversions. Several of these products have been isolated.⁵ They are all distinguished in their ¹H NMR spectra by an AB quartet around δ 6 with $J = 2.8$ Hz for the two cyclobutene vinyl protons. These vinyl protons show a coupling of ~ 1 Hz with any adjoining bridgehead protons. Heating these cyclobutenes (except that from *o*-AP₂d) for short periods at 200°C converts them quantitatively to the same cyclooctatrienes obtained by preparative GC separation of the original irradiated solutions. Irradiation for 30 min at either 313 or 365 nm of solutions 10^{-2} M in the cyclooctatriene from *o*-AP₂b caused complete conversion to the bicyclo[4.2.0]octa-2,7-diene photoproduct.

The kinetics performed on the para substituted ketones² demands two-step, reversible addition of the double bond to the para carbon of the benzene ring. Prompt closure of the original 1,4-biradicals would give formal suprafacial 2 + 2 cycloadducts with a cyclohexadiene subunit, such as have been isolated from direct photoaddition of alkenes to benzonitriles and to naphthonitriles.^{6,7} The only acetophenone that yields an isolable cyclohexadiene is *o*-AP₂d, which gives different products than do the other compounds in Chart I. The progress of its photoreaction was followed both by UV and by FT-NMR. The only photoproduct detected by NMR at 20% conversion is the bicyclo[4.2.0]octa-2,4-diene **5**.⁸ Upon extended irradiation, however, mixtures of **6** and **5** are formed until only **6** survives. Control experiments indicated that no thermal rearrangement of **5** to **6** occurs. Obviously the



first-formed cyclohexadiene is converted to the cyclobutene in a secondary photoreaction. UV analysis of reaction progress indicated early formation and eventual disappearance of an intermediate that absorbs weakly at 350 nm, which we presume is **7**. Heating the isolated **6**⁵ at 100°C for 10 min produced a small amount of **5**; heating at 120°C for 30 min produced a mixture of **5** and some AP₂d. Thus **6** does not rearrange thermally to a *stable* cyclooctatriene but to products derived from one.

We conclude that all the ketones form bicyclo[4.2.0]octa-2,4-dienes initially. These normally are not detected because they undergo rapid thermal disrotatory opening to all-cis cyclooctatrienes,⁹ which have large extinction coefficients and absorb a second photon to undergo electrocyclic closure¹⁰ to the photostable bicyclo[4.2.0]octa-2,7-dienes.¹¹ This general mechanism is shown in Scheme I. The different product distribution from *o*-AP₂d reflects a change in the cyclohexadiene-triene interconversion. There is ample precedent for *gem*-dimethyl substitution altering the *thermal* equilibrium between bicyclooctadienes and cyclooctatrienes in favor of the former.¹² As **7** is formed from **5**, the unfavorable equilibrium is offset by the irreversible photoisomerization of **7** to **6**. Upon being heated, **6** opens to **7**, which rearranges immediately to the thermodynamically preferred **5**, which is unstable thermally with respect to the starting aromatic system. The most unusual aspect of the overall mechanism, apart from the initial triplet cycloaddition itself, is the rapidity of the bicyclooctadiene-to-cyclooctatriene isomerization.

The overall quantum yield for isolated cyclooctatrienes is in the 25–30% range for *o*-AP₂a and *o*-AP₂b, despite two photoreactions being required. Therefore both photoconversions must have high quantum efficiencies. It is noteworthy that the cyclooctatriene and the bicyclo[4.2.0]octa-2,7-diene are interconverted by irradiation of the former and heating of the latter. We presume that the NMR spectra would reveal the presence of different stereoisomers of either compound. If the photoreaction obeys orbital-symmetry rules, the all-cis cyclooctatriene would undergo disrotatory closure to yield a *cis*-fused cyclobutene. NOE experiments on the cyclobutene from *o*-AP₂b do suggest a *cis* ring fusion, since there is enhancement of the vinyl proton at C-11 but not of the bridgehead proton at C-9 when the methyl (R_1) group at C-3 is irradiated. Therefore we tentatively conclude that the thermal opening of the cyclobutene is not a concerted electrocyclic reaction and probably results from the weakened character of the middle C–C bond caused by donor–acceptor conjugation.¹³ The

(3) e.g., 4-acetyl-11-oxabicyclo[8.5.0]undeca-1,3,5-triene from *p*-AP₂a: ¹H NMR (CDCl₃) δ 7.00 (d, 1 H, $J_{2,3} = 6.8$ Hz), 6.27 (d, 1 H, $J_{5,6} = 12.5$ Hz), 5.92 (m, 1 H, $J_{6,5} = 12.5$ Hz, $J_{7,6} = 6.8$ Hz), 5.40 (d, 1 H, $J_{3,2} = 6.8$ Hz), 4.24 (m, 1 H, $J_{10,10'} = 6.8$ Hz), 4.16 (m, 1 H, $J_{10,10'} = 6.8$ Hz), 3.06 (m, 1 H, $-\text{C}(8)\text{H}-$), 2.29–2.50 (m, 2 H, $-\text{C}(7)\text{H}_2-$), 1.83–2.13 (m, 2 H, $-\text{C}(9)\text{H}_2-$); ¹³C NMR (CDCl₃) δ 199.3 (C=O); IR 1680 cm⁻¹. NMR coupling constants were determined by decoupling at 250 MHz.

(4) The cyclooctatrienes are stable for weeks in a refrigerator but decompose and polymerize in days at room temperature.

(5) e.g., 1-acetyl-3-methyl-6-oxatricyclo[7.2.0.0^{3,7}]undeca-7,10-diene from *o*-AP₂b: ¹H NMR (C₆D₆) δ 6.04 (d of d, 1 H, $J_{11,10} = 2.8$, $J_{9,10} = 0.9$ Hz), 5.81 (d, 1 H, $J_{10,11} = 2.8$ Hz, cyclobutene), 4.98 (d, 1 H, $J_{8,9} = 6.6$ Hz, $\text{CH}=\text{C}-\text{O}$), 3.77 (complex m, 2 H, $\text{O}-\text{CH}_2$), 3.32 (d of d, 1 H, $J_{9,8} = 6.6$, $J_{10,9} = 0.9$ Hz, $\text{CH}-\text{CH}=\text{C}-\text{O}$), 1.85–2.00 (d of d, 2 H, $J_{2,2'} = 14$ Hz, CH_2), 1.85 (s, 3 H, CH_3CO), 1.40–1.10 (m, 2 H, $-\text{CH}_2-\text{CH}_2-\text{O}$), 1.02 (s, 3 H, CH_3); ¹³C NMR (CDCl₃) δ 208 (C=O); IR 1688 cm⁻¹; UV λ_{max} (CH₃CN) 295 nm (ϵ 200).

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(8) See footnote 19 of ref 1.

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(11) A direct sigmatropic photorearrangement of **5** to **6** is an a priori possibility but seems unlikely here, since the acetophenones absorb so strongly that the initial cyclohexadiene structures would build up much more than is observed.

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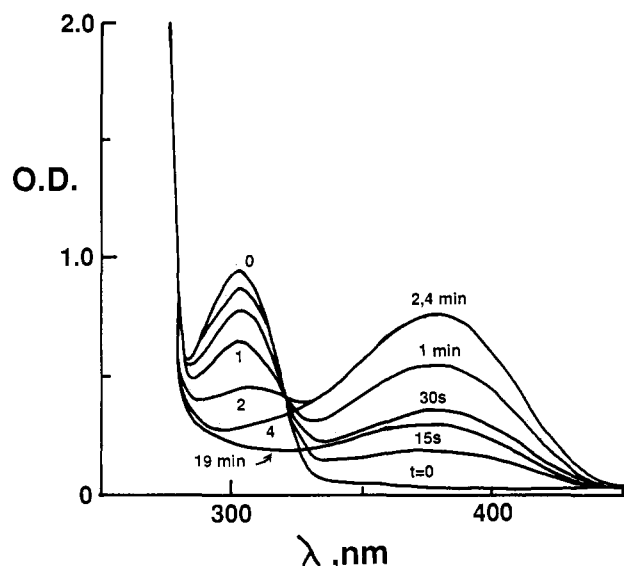
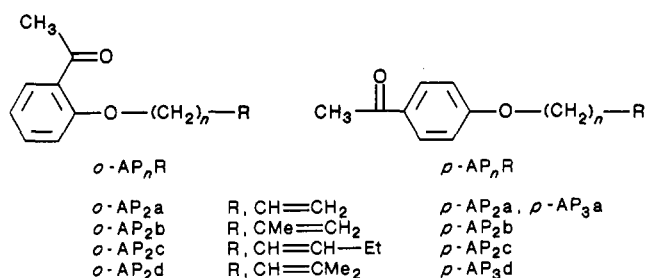
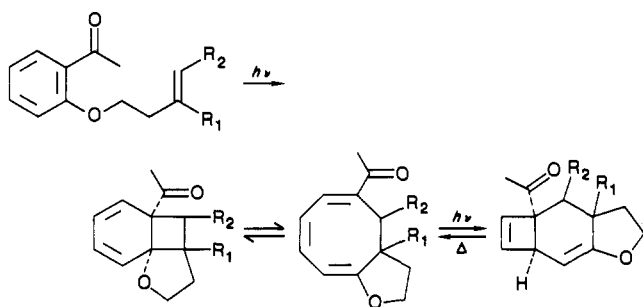


Figure 1. UV spectrum of 0.00024 M *o*-AP₂b in benzene as a function of time of 313-nm irradiation.

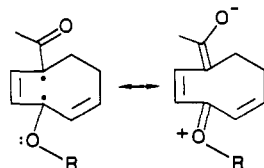
Chart I



Scheme I



same bond weakening presumably promotes the unusually rapid bicyclo[4.2.0]octa-2,4-diene to cyclooctatriene rearrangement.



In summary, intramolecular 2 + 2 cycloaddition of double bonds to the benzene ring of π, π^* triplet ketones leads in good chemical yield to bicyclo[4.2.0]octadiene and cyclooctatriene structures that can be interconverted cleanly. The carbonyl that facilitates the reaction by causing efficient intersystem crossing of the n, π^* singlet remains for further synthetic elaboration, such that the overall process appears to have considerable potential. In fact, we are now looking at the bimolecular counterpart and observe that the analogous cycloaddition indeed occurs.¹⁴ We shall report on the

(14) Irradiation of *p*-methoxyacetophenone in 1-hexene and GC collection produces a yellow compound with the characteristic NMR spectrum of a cyclooctatriene.

regioselectivity as soon as a general pattern emerges.

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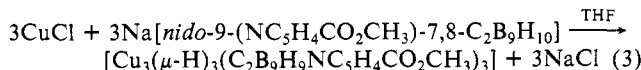
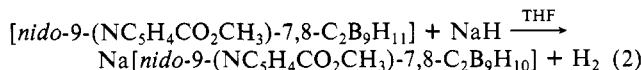
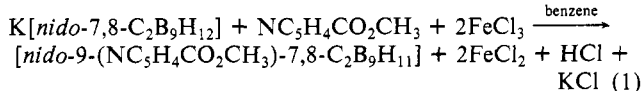
A "Clustered Cluster" with a "Pinwheel" Ligand Array. Synthesis and Structure of a Trinuclear Cupracarborane

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Recent applications of [*nido*-7,8-C₂B₉H₁₁]²⁻ (**1**)¹ in synthetic metallacarborane chemistry have resulted in novel polynuclear metallacarboranes containing M-H-B bridge bonds (M = metal). Examples include [(C₂H₅)₂Al₂(μ-H)₂(C₂B₉H₉)(C₂B₉H₁₁)],² [M₂Cu₂(μ-CO)₄(CO)₂(μ-H)₂(C₂B₉H₁₀)₂]²⁻ (M = Mo, W),³ and [(PPh₃)₂Cu₂(μ-H)₂C₂B₉H₉] (**2**).⁴ The structural diversity observed in these metallacarboranes stems from the intrinsic dualism in the electron-donor properties of **1**. As an example, the homodinuclear formal d¹⁰ copper(I) complex **2** demonstrates two diverse bonding modes: an icosahedral *closo*-Cu^IC₂B₉ cage and a copper-copper interaction supported by Cu-H-B bridge bonds. Reported herein are the synthesis and structural characterization of a "clustered cluster",³ [Cu₃(μ-H)₃(C₂B₉H₉)₃·(n-C₇H₁₆)] [**3**·(n-C₇H₁₆), L = methyl isonicotinate], containing *nido*-Cu^IC₂B₉ cages as well as Cu(I)-Cu(I) and Cu-H-B interactions.

The anaerobic reaction of **1** with 1 molar equiv of anhydrous CuCl produced glittering metallic copper and an intense blue coloration, indicating that an undesirable redox reaction had occurred.⁵ In contrast to this observation, a "charge-compensated" carborane anion, [*nido*-9-(NC₅H₄CO₂CH₃)-7,8-C₂B₉H₁₀]⁻ (**4**), generated by deprotonation of the oxidative coupling⁶ product⁷ of [*nido*-7,8-C₂B₉H₁₂]⁻ with a Lewis base, methyl isonicotinate (NC₅H₄CO₂CH₃), reacted with an equimolar amount of anhydrous CuCl in THF to give a novel tricopper "clustered cluster" **3** as outlined in eq 1-3. A deep bluish purple solution of Na·**4**



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(5) An intense blue coloration is a typical indication of the formation of [Cu(C₂B₉H₁₁)₂]²⁻: (a) Reference 1. (b) Warren, L. F., Jr.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 4823.

(6) Young, D. C.; Howe, D. V.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1969**, *91*, 859.

(7) Spectroscopic data for [*nido*-9-(NC₅H₄CO₂CH₃)-7,8-C₂B₉H₁₁]: IR spectrum (KBr): 3116 (w), 2561 (s), 2529 (s), 1731 (s), 1434 (s), 1325 (w), 1288 (s), 1244 (w), 1118 (m), 1026 (w), 959 (w), 868 (w), 830 (w), 766 (w), 687 (w) cm⁻¹. Chemical shifts upfield of the reference are designated as negative. ¹¹B{¹H} NMR (160.463 MHz) (THF, referenced to external BF₃·OEt₂ in C₆D₆): 1.3, -5.6, -16.6, -17.7, -20.2, -22.0, -27.7, -30.5, -37.7 ppm. ¹H NMR (200.133 MHz) (CD₂Cl₂, referenced to residual solvent protons = 5.32 ppm): 9.0 (d, NC₅H₄), 8.2 (d, NC₅H₄), 4.1 (s, CH₃), 2.9 (s, carborane CH), 2.2 (s, carborane CH), -2.7 (br, B-H-B) ppm.