Table II. Geometric Properties of Selected "Dimer" and "Tetramer" Platinum Complexes[a]

		α-pyridone		1-methylthymine		1-methyluracile
	1	dimer-of-dimer[14]	blue[3,4]	head-to-tail dimer[12]	head-to-head dimer[13]	head-to-tail dimer[16]
Pt-Pt, Å	3.131	2.88	2.77	2.97	2.91	2.95
	3.204	3.13	2.88			5.10
$Pt-NH_3$ (av), Å	2.04	2.05	2.06	2.06		2.05
Pt-N (av), Å	2.00	2.05	2.05	2.04		2.05
Pt-O (av), Å	2.05	2.04	2.04	2.03		2.05
ϕ,[b] deg	38.6	30.0	27.4	36.1	29.5	35.8

[a] All the complexes are platinum(II) complexes but the α-pyridone blue, platinum oxidation state 2.25. [b] Tilting angle between adjacent Pt coordination planes.

microneedles of **1**. The yield was 0.576 g (85%) within 1-2 days. Slow recrystallization from water gave crystals up to 0.5 mm long. They have the composition[23] $[Pt_2(NH_3)_4(C_4H_5N_2O_2)_2]_2(NO_3)_4 \cdot H_2O$.

The structure of the molecular cation is shown in Figure 1, and selected interatomic distances and angles are given in Table I. It may be regarded as a dimer-of-dimer, the two dimeric units being related through an inversion center. In each dimer, two roughly planar[24] *cis*-diammineplatinum(II) units are bridged in the cis position by two deprotonated ligands arranged head-to-head. Linkage of the two dimers is achieved by intrachain hydrogen bonds between the coordinated ammines of one dimer and the oxygen atoms of the neighboring dimer. The molecular cation is surrounded by four nitrate anions and a water molecule, leading to a platinum formal oxidation state of 2 in accordance with its diamagnetic behaviour.

In Table II, structural parameters of selected "dimer" and "tetramer" platinum complexes are compared. As expected for a platinum(II) species, the Pt-Pt distances in **1** are rather long. They are similar to those found in the *cis*-diammineplatinum(II) pyrophosphate dimer (3.229 and 3.11 Å)[25] but are somewhat longer than those observed for the platinum(II) α-pyridone dimer-of-dimer.[14] The lengthening is more pronounced for the bridged Pt-Pt distance than for the nonbridged one, and this causes the two metal-metal distances occurring in a tetramer unit to differ by only 0.07 Å. This lengthening of the Pt-Pt distance offers an explanation for the exclusive formation of **1** in the reaction of 1-methylhydantoin with *cis*-diammineplatinum(II) since it may reasonably be assumed that, in the partially oxidized compound **2**, the Pt-Pt distance would present a much shorter value (ca. 2.7-2.8 Å) to accomplish metal-metal interaction. The need of drastic conditions for converting **1** into **2** and the very low stability of **2** in solution support this rationale. However, the reasons for this lengthening still remain unclear. They do not originate in geometric requirements of the five-membered ligand since the N···O bite distance (average 2.4 Å) would easily accommodate a shorter Pt-Pt distance. Moreover the discrepancy between these two distances causes the canting of the adjacent coordination planes to be longer than in the other related dimers or tetramers reported so far (cf. Table II). Furthermore, short Pt-Pt distances (ca. 2.7 Å) have recently been found in a tan compound (platinum oxidation state 2.5) formed by a five-membered heterocyclic ligand, α-pyrrolidone.[26] A possible clue to the origin of this lengthening may lie in the occurrence of a repulsive interaction between the NH_3 and NCH_3 groups within each dimer.

Finally, the particular behaviour of 1-methylhydantoin has to be emphasized since it reacts with $[Pt(NH_3)_2]^{2+}$ to yield, almost quantitatively, a nonblue product, whereas similar ligands (pyrimidines, α-pyridone, α-pyrrolidone, hydantoin) chiefly lead to blue or tan species. Thus, this ligand allows a tetranuclear array of platinum atoms to form readily but disfavors the subsequent conversion into a partially oxidized species. In this respect, compound **1** can be viewed as a borderline case among the nonblue species. Other details of the structure and solution properties will be published later.

Acknowledgment. We thank Dr. Jean Galy for the interest he has taken up in this problem. The CNRS, DESR, and DGRST have financially supported this work.

Registry No. 1, 83710-06-9.

Supplementary Material Available: Atomic positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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[23] Anal. Calcd for $PtC_4H_{11.5}N_5O_{5.25}$: C, 11.75; H, 2.84; N, 17.13; Pt, 47.73. Found, C, 11.67; H, 2.51; N, 17.21; Pt, 47.58.

[24] There is some distortion of the coordination planes; each platinum atom lies ca. 0.1 Å out of the best plane through the corresponding ligand atoms.

[25] Stanko, J. A.; Cleare, M. J. In "Platinum Coordination Complexes in Chemotherapy"; Connors, T. A., Roberts, J. J., Eds.; Springer-Verlag: New York, 1974; pp 24-26.

[26] Matsumoto, K.; Furva, K. *J. Am. Chem. Soc.* **1982**, *104*, 897-8998.

Intramolecular [6 + 4] Cycloadditions: Intramolecular Control of Periselectivity

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Intramolecular cycloadditions are versatile methods for polycyclic natural product synthesis that often proceed with pronounced regioselectivity and stereoselectivity to generate bicyclic systems with the production of four new chiral centers.[1-3] We have expanded this repertoire beyond the usual six π electron cases to intramolecular cycloadditions involving ten π electrons. We report the intramolecular [6 + 4] cycloaddition and examples of side-chain and substituent control of regioselectivity and periselectivity in intramolecular cycloadditions.

Following the techniques developed for intramolecular Diels-Alder cycloadditions of *o*-xylylenes,[4,5] we have prepared a benzocyclobutene with a suitably disposed fulvene side chain by the method shown in Scheme I. Alkylation of cyanobenzocyclobutene,[6] **1**, with LDA and 5-chloro-2-pentanone ethylene ketal in THF containing HMPA gave **2** (70%), which was deprotected with acid and converted to the fulvene with sodium cyclopentadienide in THF to give **3**, a light yellow oil,[7] in 56% yield.

The fulvene **3** was heated at 180 °C in *o*-dichlorobenzene for 7 h to produce an inseparable mixture of cyclopentadiene isomers, **4**, in 60% yield (Scheme II). The major product, **4a**, has a methyl

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[1] Reviews: Carlson, R. G. *Ann. Rep. Med. Chem.* **1974**, *9*, 270. Oppolzer, W., *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. Brieger, G.; Bennett, J. M. *Chem. Rev.* **1980**, *80*, 63.

[2] Padwa, A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 123.

[3] Wender, P. A.; Howbert, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 688.

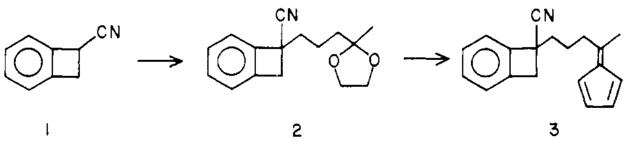
[4] Kametani, T.; Nemoto, H. *Tetrahedron*, **1981**, *37*, 3.

[5] Oppolzer, W. *Synthesis* **1978**, 793.

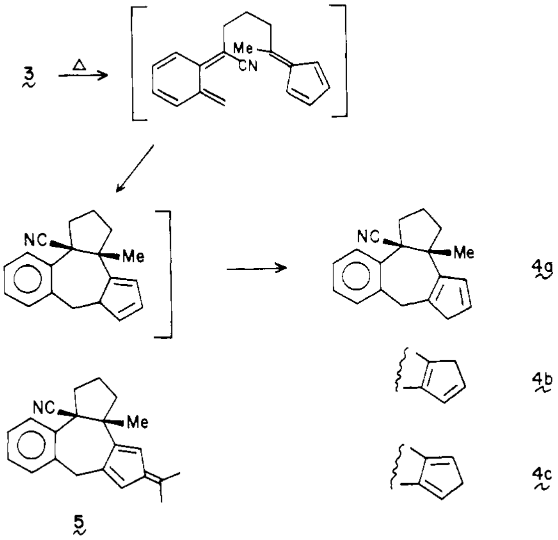
[6] Skorcz, J. A.; Robertson, J. E. *J. Med. Chem.* **1965**, *8*, 255.

[7] All new compounds gave elemental analyses, or exact masses, and spectral data in accord with the assigned structures.

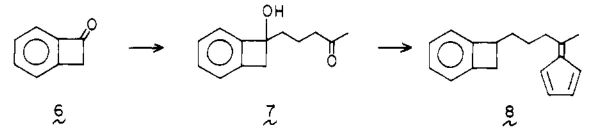
Scheme I



Scheme II



Scheme III



resonance in the 300-MHz NMR spectrum at δ 1.46, cyclopentadiene olefinic hydrogen resonances at δ 6.15 and 6.32, and a pair of methylene doublets at δ 3.65 and 4.23 with $J = 17.4$ Hz. The minor isomers, **4b** and **4c**, have similar spectra, with resonances slightly offset from those of **4a**. The methyl groups in **4a** and **4b** appear at δ 1.52 and 1.66. The ratio of methyl intensities, 4.0:1.7:1.0, is indicative of the ratio of cyclopentadiene isomers.[8]

In order to confirm the structural assignment, the mixture **4a–c** was converted into a single fulvene, **5**,[7] by treatment with KOH and acetone. The light yellow fulvene is an oil which has methyl resonances at δ 1.69, 2.09 and 2.10.

The cis fusion present in **4** and **5** was inferred from the relatively low-field positions of the quaternary methyl group resonances, which indicates that these methyl groups reside in the deshielding zone of the vicinal cyano group.[9] Selective cis-Diels–Alder cycloadditions are also observed for *o*-xylylenes connected to an alkene by a three-atom chain.[5]

The benzocyclobutene must open to give the *Z* isomer,[5,10] but the cis stereochemistry does not establish in this case whether the cycloaddition is endo or exo. Other [6 + 4] cycloadditions of fulvenes proceed with exclusive exo stereochemistry,[11] as predicted by secondary orbital interactions.[12] However, the steric requirements of the forming five-membered ring, particularly in the canted arrangement of the planes of the cycloaddend moieties,[13] and the attractive secondary orbital interactions that can occur for this reaction lead us to propose that this intramolecular [6 + 4] cycloaddition occurs through the endo-transition state (see below).

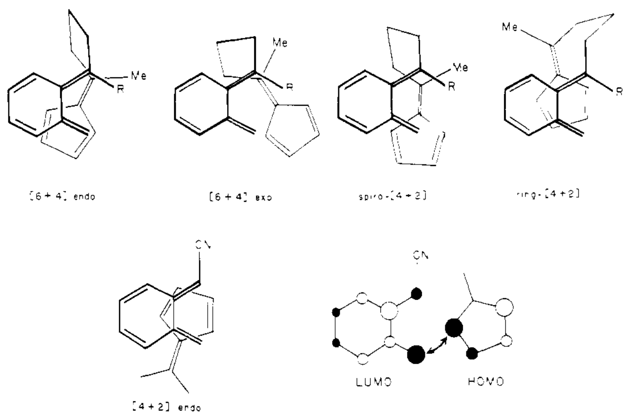
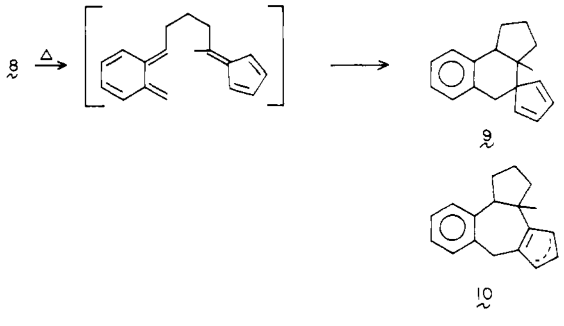


Figure 1. Transition structures for the intramolecular [6 + 4], spiro-[4 + 2], and ring-[4 + 2] cycloadditions. The intermolecular endo-[4 + 2] transition structure is sketched on the lower left. The relevant frontier molecular orbitals for the cyano-substituted case are shown at the lower right.

Scheme IV



In order to establish whether the cyano group has a significant influence upon the intramolecular [6 + 4] periselectivity observed for reactions of **3**, we synthesized the hydrocarbon analogue as shown in Scheme III. The reaction of benzocyclobutenone[15] with the Grignard reagent formed from 5-chloro-2-pentanone ethylene ketal in THF followed by deprotection in the acid workup gave the keto alcohol **7** (69%), which was dehydrated with absolute oxalic acid in toluene (51%). Catalytic hydrogenation (89%) followed by fulvene formation with cyclopentadiene and 40% aqueous methylamine[16] gave **8** (51%).

The fulvene **8** was heated in toluene at 195 °C for 12 h to produce the spiro compound **9** (26%, Scheme IV) and an inseparable mixture of [6 + 4] cyclopentadiene isomers, **10** (44%). The minor product, **9**, has a methyl resonance at δ 0.90, a pair of methylene doublets at δ 2.39 and 3.44 ($J = 17.6$ Hz), cyclopentadiene resonances at δ 6.30–6.43 (2 H) and 6.50 (2 H), and cyclopentane resonances at δ 1.2 and 2.2 (6 H). The methine proton appears at δ 2.99 (dd, $J = 8.1, 11.5$ Hz). We have no direct evidence as to the cis or trans nature of this adduct.

The major cyclopentadiene isomer of **10** has a methyl resonance at δ 0.67, a methine resonance at δ 3.5, and remaining resonances similar to those of **4**. The cis or trans nature of this adduct has not been proven.

The intramolecular [6 + 4] cycloadditions observed for **3** and **8** contrast with the analogous intermolecular cases, which give

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(8) On the basis of the long-range coupling constants and expected relative stabilities of cyclopentadiene isomers (Mironov, V. A.; Ivanov, A. P.; Kimelfeld, Ya. M.; Petrovskaya, L. T.; Akhrem, A. h. *Tetrahedron Lett.* **1969**, 3347), we tentatively assign structures **4a–c**, shown in Scheme II, to the major, intermediate, and minor isomers, respectively.

(9) Onda, M.; Gotoh, M.; Okada, J. *Chem. Pharm. Bull.* **1975**, *23*, 1561.

(10) Kametani, T.; Tsubuki, M.; Shiratori, Y.; Kato, Y.; Nemoto, H.; Ihara, M.; Fukumoto, K.; Satoh, F.; Inoue, H. *J. Org. Chem.* **1977**, *42*, 2672. Kametani, T.; Kato, Y.; Honda, T.; Fukumoto, K. *J. Am. Chem. Soc.* **1976**, *98*, 8185.

(11) See, for example: Paddon-Row, M. N.; Watson, P. L.; Warrener, R. N. *Tetrahedron, Lett.* **1973**, 1033.

(12) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 4388.

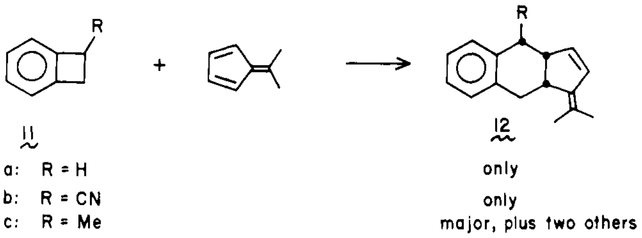
(13) Townsend, R. E.; Ramunni, G.; Segal, G.; Hehre, W. J.; Salem, L. *J. Am. Chem. Soc.* **1976**, *98*, 2190.

(14) Bimanand, A. Z.; Gupta, Y. N.; Doa, M.; Eaton, T. A.; Houk, K. N.; Fronczek, F. R. *J. Org. Chem.*, in press.

(15) O'Leary, M. A.; Stringer, M. B.; Wege, D. *Aust. J. Chem.* **1978**, *31*, 2003.

(16) Freiesleben, W. *Angew Chem., Int. Ed. Engl.* **1963**, *2*, 396.

only endo [4 + 2] adducts **12a** and **12b**, respectively,[14] as are observed for other Diels–Alder reactions of this *o*-xylylene.[17] This alteration in periselectivity may be rationalized primarily on the basis of conformational requirements in the ring, which is formed from the connecting side chain. As shown in Figure 1, the endo [6 + 4] cycloaddition can occur with the forming five-membered ring in a favorable envelope conformation. This transition state can also benefit from favorable secondary orbital interactions. The exo-cis transition structure must have a more strained developing five-membered ring. The spiro-[4 + 2] transition structure has a slightly less favorable conformation of the forming cyclopentane ring than the endo-[6 + 4]. In Figure 1, we have shown the spiro-[4 + 2] transition structure leading to the cis product, although the trans transition state is quite similar with respect to side-chain conformation. In the four possible transition structures that can give [4 + 2] adducts on a fulvene ring double bond, a cycloheptene is formed from the side chain. The most reasonable of these, a endo-cis transition structure, is disfavored by the partial eclipsing interactions that must develop in the forming cycloheptene ring.



These side-chain conformational effects make the [6 + 4] adduct preferable to the spiro-[4 + 2] and disfavor the ring-[4 + 2], whereas the intermolecular case (**11**, R = Me) produces these three adducts in 18%, 9%, and 50% yield, respectively.[14] The parent, **11a**, and cyano derivative, **11b**, give only the ring-[4 + 2] adducts, **12**. The [6 + 4] and spiro-[4 + 2] adducts are favored by xylylene HOMO–fulvene LUMO interactions, while the ring-[4 + 2] adduct is favored by xylylene LUMO–fulvene HOMO interactions,[18] which dominate for fulvenes and simple dienes in intermolecular cases.[18]

The cyano substituent shifts the reaction to [6 + 4] exclusively. This contrasts to the intermolecular case, which produces the endo-[4 + 2] adduct, **12b**, from the transition structure shown in Figure 1, as expected from maximization of the xylylene LUMO–fulvene HOMO overlap. The relevant frontier molecular orbitals are shown at the bottom of Figure 1. In the intramolecular reaction, the stabilizing interaction between C-4 of the diene and C-1 of the fulvene cannot be attained in any sterically feasible [4 + 2] transition state, and only the [6 + 4] cycloaddition is observed, in spite of the node through C-6 in the fulvene HOMO. Thus, intramolecular [6 + 4] cycloadditions of dienylfulvenes, joined at C-1 of the diene and C-6 of the fulvene, compete favorably with [4 + 2] cycloadditions. This tendency is accentuated when the diene is substituted by an acceptor substituent at C-1, as found here, and should also be favored by a donor at C-4, as found in intermolecular cases.[19]

We are exploring the generality of intramolecular 10 π electron cycloadditions for the synthesis of natural products containing a hydroazulene fused to an additional ring.

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Registry No. 1, 6809-91-2; **2**, 83692-94-8; **3**, 83692-95-9; **4a**, 83692-96-0; **4b**, 83692-97-1; **4c**, 83692-98-2; **5**, 83692-99-3; **6**, 3469-06-5; **7**, 83693-00-9; **8**, 83693-01-0; **9**, 83693-02-1; **10** (isomer 1), 83693-03-2; **10** (isomer 2), 83693-04-3; 5-chloro-2-pentanone ethylene ketal, 5978-08-5.

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[17] Franck, R. W.; John, T. V. *J. Org. Chem.* **1980**, *45*, 1470 and references therein.

[18] Houk, K. N.; George, J. K.; Duke, R. E., Jr. *Tetrahedron* **1974**, *39*, 523. Houk, K. N.; Luskus, L. J. *J. Org. Chem.* **1973**, *38*, 3836.

[19] Dunn, L. C.; Chang, Y.-M.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 7095. Dunn, L. C.; Houk, K. N. *Tetrahedron Lett.* **1978**, 3411. Mukherjee, D.; Dunn, L. C.; Houk, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 251.

Intramolecular Addition of an Aliphatic C–H Bond to a Tantalum–Carbon Double Bond

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The high valent, Early transition metal to carbon double bond (alkylidene), despite being a relatively new functionality is nevertheless an important group.[1] It has been shown to be the active species in olefin metathesis[2] and implied as a key intermediate in olefin polymerization.[3] Other, stoichiometric reactions of this group include Wittig-type functionalizations of ketones and imines,[4] insertion of carbon monoxide to yield ketenes,[1] and hydrogenation under mild conditions to alkane.[1] Recently, the migratory insertion of a number of groups to alkylidene ligands have been characterized.[5,6] We report here our observation that intramolecular addition of an aliphatic CH bond to a tantalum alkyidene can be facile, implying a possible potential of this function for CH bond activation.

We recently reported the synthesis of the alkylidene compound $Ta(OAr')_2(=CHSiMe_3)(CH_2SiMe_3)$ (I) from the reaction of $Ta(OAr')_2Cl_3$ (OAr′ = 2,6-di-*tert*-butylphenoxide) with 3 equiv of $LiCH_2SiMe_3$.[7] A single-crystal X-ray diffraction study of I has been carried out, and the resulting structure along with the atom numbering scheme and some pertinent bond distances and angles are shown in Figure 1.[8] The molecule can be seen to possess an approximately tetrahedral geometry about the metal, but with some distortions. The angle between the sterically demanding aryl oxide ligands has opened up to 127°, while that between the two organic functions has been compressed. The Ta–OAr′ distances are short (Figure 1), implying that a considerable amount of oxygen to tantalum π bonding is taking place. The tantalum–alkylidene distance is consistent with previously characterized alkylidene complexes of this type.[1] The orientation

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[1] Schrock, R. R. In "Reactions of Coordinated Ligands"; Braterman, P. S., Ed; Plenum Press: New York, 1982.

[2] Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1.

[3] (a) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604. (b) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331.

[4] (a) Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399. (b) Rocklage, S.; Shrock, R. R. *Ibid.* **1980**, *102*, 7808.

[5] Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organo-transition Metal Chemistry"; University Science: California, 1980.

[6] Hayes, J. C.; Pearson, G. D. N.; Cooper, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 4648.

[7] Chamberlain, L.; Keddington, J.; Rothwell, I. P. *Organometallics* **1982**, *1*, 1098.

[8] Crystal data for $Ta(OC_{14}H_{21})_2(=CHSiMe_3)(CH_2SiMe_3)$ at −162 °C: space group = $P2_1/c$; a = 11.037 (4), b = 25.402 (15), c = 17.113 (7) Å; β = 126.69 (2)°; Z = 4; d_c = 1.321 g·cm^{-3}. Of the 3605 unique reflections collected with use of Mo Kα radiation ($6° \le 2\theta \le 40°$), the 2450 having $F > 2.33\sigma(F)$ were used in the full-matrix refinement. Final residuals are R_F = 0.0802 and R_{wF} = 0.0677.