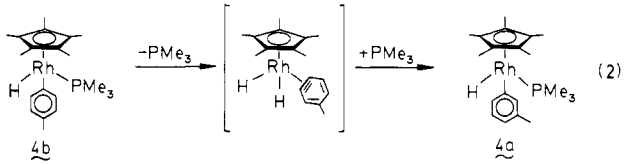
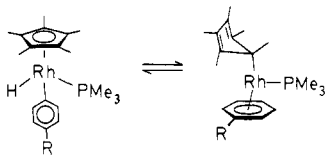
$\{[C_5(CH_3)_5]Rh(p\text{-}C_6H_4CH_3)(THF\text{-}d_8)[P(CH_3)_3]\}^+$ (**5**). Treatment of this solution of **5** with 1 equiv of $Li^+[HB(s\text{-}Bu)_3]^-$ at −40 °C followed by warming to −25 °C in the probe of an NMR spectrometer showed ~90% conversion to the hydrido derivative **4b**. The interconversion of **4b** to **4a** was observed upon warming the solution to −10 °C, giving an equilibrium **4a**/**4b** ratio of 2:1 (Figure 1).

The above experiments indicate that facile interchange of the site of attachment of the aromatic ligand to the metal occurs at −10 °C *without dissociation of the arene*. The most plausible mechanism for this isomerization involves a reductive elimination process to form **6** in which the arene remains coordinated to the metal in an η^2 fashion (Scheme II). An alternative mechanism, involving phosphine dissociation and formation of a dihydridobenzyne complex (eq 2), could also explain the observed isomerization of **4a** and **4b** at −10 °C.[12] However, no phosphine exchange is observed upon treatment of **3** with $P(CD_3)_3$ in C_6D_6 after 1 h at 25 °C, thereby ruling out this possibility. Another possible mechanism would involve shifting the $C_5(CH_3)_5$ ring from η^5 to η^1 coordination while forming an η^6-arene complex (eq 3).



(2)



(3)

This variation in cyclopentadienyl coordination has been postulated[13] and observed[14] by others in intermolecular reactions of ligands with cyclopentadienyl complexes. However, when $[(C_5(CH_3)_5]Rh[P(CH_3)_3](H)(C_6D_5)$ is prepared at −20 °C in THF-d_8 and then allowed to warm to −10 °C, the aromatic region of the ^1H NMR shows rapid growth of a singlet at δ 7.27 (H_{ortho}) followed by singlets at δ 6.70 (H_{meta}) and 6.67 (H_{para}). These observations clearly rule out an η^6-arene intermediate[15] and offer strong support for the η^2-arene sequence shown in Scheme II.

The observation of intermolecular arene exchange only above 60 °C indicates that arene dissociation from the metal to form the coordinatively unsaturated complex $[C_5(CH_3)_5]Rh[P(CH_3)_3]$ (**7**) is a kinetically unfavorable process with respect to the oxidative addition and reductive elimination to arene C–H bonds. The only other report of arene precoordination followed by intramolecular C–H activation involves the complex $(\eta^6\text{-}C_6H_6)Os(C_2H_4)[P(CH_3)_3]$, in which arene dissociation is quite unfavorable.[16]

In order to evaluate the barrier to arene coordination in the reaction of **7** with benzene, a solution of $[C_5(CH_3)_5]Rh[P(CH_3)_3](H)_2$[17] in C_6D_6 was irradiated at 25 °C with a medium-pressure Hg lamp. ^1H NMR spectra showed the disappearance of the dihydride and the appearance of resonances at δ 1.79 (d, J = 1.4 Hz, 15 H) and 0.90 (d, J = 9.8 Hz, 9 H) attributable to $[C_5(CH_3)_5]Rh[P(CH_3)_3](D)(C_6D_5)$, indicating a low barrier for arene coordination to **7**.

In conclusion, facile oxidative addition and reductive elimination of arene C–H bonds occurs in these permethylcyclopentadienyl rhodium complexes at or below room temperature, while dissociation of an η^2-bound arene requires heating to 60 °C. The coordinatively unsaturated intermediate **7**, on the other hand, reacts rapidly with arene C–H bonds to produce aryl hydrides, indicating that arene coordination plays an important role in the oxidative-addition reaction. Studies are underway to elucidate the importance of this coordination in arene activation and its relevance to alkane activation.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Camille and Henry Dreyfus Foundation for support of this research. We also thank Johnson Matthey, Inc., for a generous loan of rhodium trichloride.

Registry No. 1, 81971-44-0; **2**, 81971-45-1; **3**, 81971-46-2; **4a**, 81971-47-3; **4b**, 81971-48-4; **5**, 81971-49-5; $[C_5(CH_3)_5]RhCl_2[P(CH_3)_3]$, 80298-79-9.

(12) Compare: Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650–6667.
(13) Crichton, O.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1980**, 167–173. Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27–35.
(14) Casey, C. P.; Jones, W. D. *J. Am. Chem. Soc.* **1980**, *102*, 6154–6156. Casey, C. P.; Jones, W. D.; Harsey, S. G. *J. Organomet. Chem.* **1981**, *206*, C38–42.
(15) Alternatively, an $[\eta^3\text{-}C_5(CH_3)_5]Rh[P(CH_3)_3](\eta^4\text{-}C_6H_5D)$ complex could be postulated as an intermediate. However, the rapid initial formation of the ortho-H phenyl-d_4 species rules out this mechanism also.
(16) Werner, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 793–794.
(17) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003–2008.

Metallacyclobutane to Metallacyclopentane Ring-Expansion Reactions

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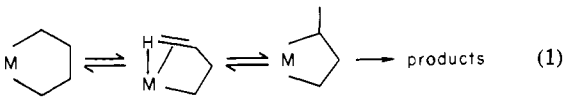
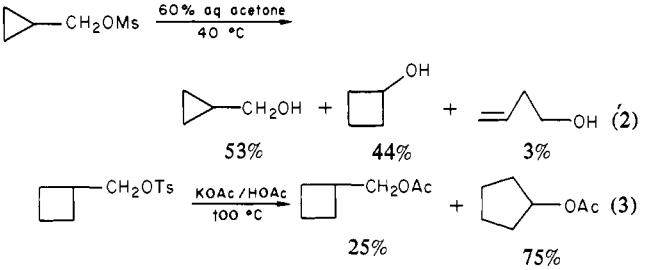
Although there is much interest in metallacycles $M(CH_2)_n$ due to their proposed roles as intermediates in transition-metal-catalyzed reactions, few examples of interconversion between metallacycles of order n and $n + 1$ are known.[1,2] Schrock has proposed that short-lived tantalacyclobutane intermediates are formed from tantalacyclopentanes during some catalytic alkene dimerization reactions (eq 1),[1] but the reverse reaction, which should be favored thermodynamically,[2,3] has not been observed.[4]



(1)

We report the first examples of metallacyclobutane to metallacyclopentane ring-expansion reactions in which both starting materials and products are isolable crystalline solids. Our approach was based on analogy with the solvolysis of cyclopropylmethyl or cyclobutylmethyl esters which occurs with at least partial rearrangement to cyclobutyl or cyclopentyl derivatives, respectively[5-7] (eq 2 and 3, OMs = mesylate, OTs = tosylate).

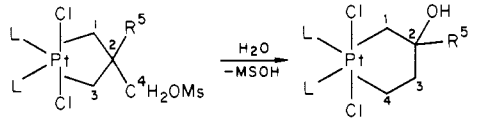


(2) (3)

(1) McLain, S. J.; Sancho, J.; Schrock, R. R., *J. Am. Chem. Soc.* **1979**, *101*, 5451.
(2) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948.
(3) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149.
(4) This is perhaps surprising since partial β-elimination from α-methyl substituents of platinacyclobutanes has been reported to occur under conditions where platinacyclopentane products (eq 1) would be expected to be thermally inert: Johnson, T. H.; Cheng, S.-S. *J. Am. Chem. Soc.* **1979**, *101*, 5277.
(5) Majerski, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 665.

0002-7863/82/1504-4242$01.25/0

Complexes Ia–c were prepared from the corresponding cyclopropanes by conventional methods[3] and were fully characterized.[8] Each was then solvolyzed in 60% v/v acetone-d_6/D_2O at 36 °C. The solvolyses, which were monitored by ^1H NMR spectroscopy, followed pseudo-first-order kinetics with $k_{obsd} = 2.4 \times 10^{-5}$, 5.9×10^{-6}, and 1.8×10^{-5} s^{-1} for Ia, Ib, and Ic, respectively. The products, formed in very high yield, were identified as IIa–c, respectively (eq 4).[9]



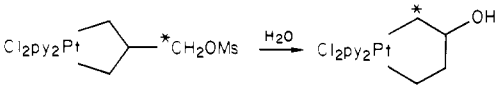
(4)

Ia, L = py; R = H
Ib, L_2 = 2,2′-bipy; R = H
Ic, L = py; R = Me

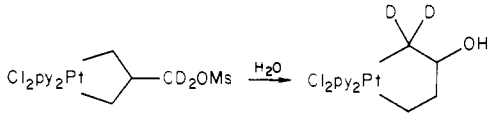
IIa, L = py; R = H
IIb, L_2 = 2,2′-bipy; R = H
IIc, L = py; R = Me

In the solvolysis of Ia, the product contained IIa but also two further isomers, identified by ^{13}C NMR spectroscopy,[10] differing only in the orientation of chloride and pyridine ligands with respect to the platinacyclopentane ring. Similar isomers have been observed previously in related platinacyclopentanes.[11] However, IIb and IIc were formed essentially as single isomers, presumably those shown in eq 4. In no case was the platinacyclobutane derivative $[PtCl_2L_2\{CH_2CR(CH_2OH)CH_2\}]$ formed in detectable quantity,[12] and hence solvolysis occurs with essentially complete ring expansion. Of particular value in the unequivocal characterization of the platinacyclopentane products were the multiplicities observed in the off-resonance decoupled ^{13}C NMR spectra[8-10] in the magnitudes of the couplings $^1J_{PtC}$, which differ markedly in platinacyclobutanes[3] and platinacyclopentanes.[13]

Some insight into the mechanism of the ring expansion is gained by studying the rearrangement of specifically labeled derivatives of Ia as shown in eq 5, where *C represents a carbon center enriched with ^{13}C to an extent of 7.5%, and eq 6.[14]

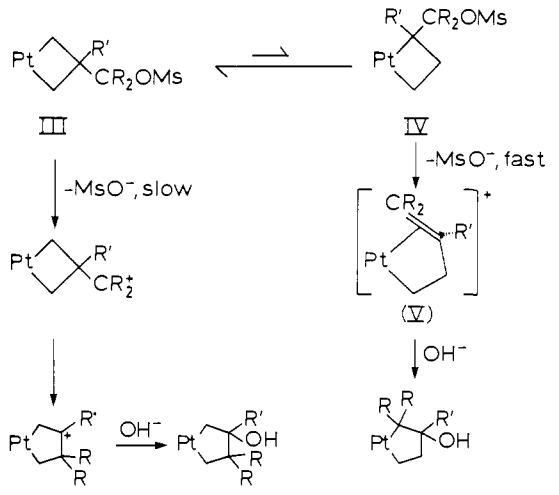


(5)



(6)

Scheme I



The selectivities observed are not expected by analogy with the solvolyses of cyclopropylmethyl and cyclobutylmethyl esters, in which general scrambling of methylene groups occurs in the intermediate carbonium ions.[6,7] In addition, the labels can only appear in the positions found (eq 5 and 6) if skeletal isomerization[3] of the platinacyclobutane occurs prior to hydrolysis and if no hydride shifts occur. Thus the mechanism shown in Scheme I is strongly indicated (chloride and pyridine ligands omitted[15]).

In the solvolysis of cycloalkylmethyl esters, the rate of reaction is largely influenced by the degree of strain in adjacent C–C bonds. The rate constant for hydrolysis of $CH_2CH_2CH_2CH_2OMs$ in 60% aqueous diglyme at 40 °C is 2.607×10^{-3} s^{-1},[16] and by extrapolation from rates at higher temperatures, that for acetolysis of cyclobutylmethyl tosylate at 36 °C is expected to be $\sim 3 \times 10^{-7}$ s^{-1}.[17] Since platinacyclobutanes are less strained than cyclobutanes,[2,3] the solvolysis rate of III (Scheme I) could be predicted to be less than 3×10^{-7} s^{-1} under the conditions used, and it is therefore not surprising that this reaction occurs to only a minor extent. Ionization of IV gives the stabilized but-3-enylplatinum(IV) species V, and the solvolysis is thus greatly accelerated. Since less than 2% of isomer IV is present, the true rate of solvolysis of IV must be very much greater than the overall observed solvolysis rate.[18,19]

(6) Shatkina, T. N.; Leont'eva, E. V.; Lippmaa, E. T.; Pekhk, T. I.; Rentov, O. A. *Dokl. Akad. Nauk SSSR* **1972**, *207*, 1144.

(7) This topic has been the subject of reviews: Richey, H. G., Jr.; Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III In "Carbonium Ions"; vol. III, Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III, pp 1201 and 1295.

(8) Characterization by elemental analysis and ^1H and ^{13}C NMR spectroscopy. For example, Ia in $CDCl_3$ gives the following ^{13}C NMR parameters: δ −13.67 (C^1, C^3, $^1J_{PtC}$ = 356 Hz), 42.1 (C^2, $^2J_{PtC}$ = 104 Hz), 73.8 (C^4, $^3J_{PtC}$ = 54 Hz), 37.1 ($MeSO_3$).

(9) For example, IIb in CD_2Cl_2 solution gives the following ^{13}C NMR parameters: δ 33.1 (C^1, t, $^1J_{PtC}$ = 540 Hz), 77.2 (C^2, d), 40.7 (C^3, t), 20.9 (C^4, t, $^1J_{PtC}$ = 494 Hz). IIc in CD_2Cl_2 solution gives δ 34.0 (C^1, t, $^1J_{PtC}$ = 541 Hz), 81.0 (C^2, s, $^2J_{PtC}$ = 15 Hz), 46.9 (C^3, t, $^2J_{PtC}$ = 6 Hz), 18.4 (C^4, t, $^1J_{PtC}$ = 494 Hz), 25.7 (C^5, q, $^3J_{PtC}$ = 34.5 Hz). In addition the elemental analyses, IR, ^1H NMR, and mass spectra of the complexes confirm the proposed structures for IIa–c. NMR spectra of crude reaction mixtures show no detectable platinacyclobutanes, and isolated product yields were typically 80% after purification.

(10) IIa and its isomers in $CDCl_3$ or CD_2Cl_2 give the following ^{13}C NMR parameters: δ 28.8 (C^1, t, $^1J_{PtC}$ = 537 Hz), 76.9 (C^2, d), $^2J_{PtC}$ = 20 Hz), 40.8 (C^3, t), 18.1 (C^4, t, $^1J_{PtC}$ = 494 Hz), (peaks attributed to isomer IIa); δ 24.9 (C^1, t, $^1J_{PtC}$ = 534 Hz), 80.3 (C^2, d), 81.0 (C^2, d), 37.4 (C^3, t), 38.0 (C^3, t), 10.9 (C^4, t, $^1J_{PtC}$ = 476 Hz) (peaks attributed to two of the five other geometrical isomers with accidental coincidence of δ (C^1) and (C^4)). The relative amounts of IIa and the other geometrical isomers differed appreciably in different syntheses.

(11) Brown, M. P.; Hollings, A.; Houston, K. J.; Puddephatt, R. J.; Rashidi, M. *J. Chem. Soc., Dalton Trans.* **1976**, 786.

(12) These platinacyclobutanes have been prepared independently and fully characterized. In favorable cases, e.g., in solvolysis of Ia, this product would have been detected if present in 1–2% yield.

(13) Barber, G. K.; Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1839.

(14) As in solvolysis of Ia, each product was formed as a mixture of three isomers. Positions of labels were determined unambiguously from the ^{13}C NMR spectra, by comparison with the spectra of IIa. In the more sensitive case with ^{13}C labeling, a minor amount of product with label at C^3 was detected. This is estimated to comprise about 15% of the total.

(15) It is possible that ligand dissociation of chloride or pyridine may occur at intermediate stages. This aspect of the mechanism has not yet been investigated. Ligand dissociation is known to be necessary during the skeletal isomerization of platinacyclobutanes.[3] These ancillary ligands are therefore omitted in the scheme. We emphasize that, since the solvolysis is irreversible, the results reported herein are not directly relevant to the problem of how great a difference in ring strain there is between platinacyclobutanes and platinacyclopentanes, but this aspect will be discussed elsewhere. The high preference for ring expansion could be a kinetic effect due to a preference for nucleophilic attack at the β-carbon of V.

(16) Goricnik, B.; Majerski, Z.; Borcic, S.; Sunko, D. E. *J. Org. Chem.* **1973**, *38*, 1981.

(17) Wiberg, K. B.; Hess, B. A. *J. Am. Chem. Soc.* **1966**, *88*, 4433.

(18) The solvolysis rate for IV may be comparable with that for cyclopropylmethyl mesylate.[16] However, a mechanism in which dissociation of cyclopropane occurs followed by solvolysis and oxidative addition of the cyclobutanol can be eliminated, since neither cyclopropanes nor cyclobutanes react with $[PtCl_2py_2]$.

(19) The observation that Ib is solvolyzed four times more slowly than Ia is significant. It has been shown that chelate ligands greatly retard the required skeletal isomerization of platinacyclobutanes.[3] At least for Ib it is possible that skeletal isomerization could be rate determining or that solvolysis of III might be dominant. This aspect is being investigated further.

Acknowledgment. We thank NSERC (Canada) for financial support, NATO for a travel grant, and Johnson Matthey Ltd. for the loan of platinum compounds. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Some NMR data were obtained at the Southwestern Ontario NMR Centre, funded by NSERC.

Registry No. Ia, 81875-81-2; Ib, 81875-82-3; Ic, 81875-83-4; IIa, 81875-84-5; IIb, 81875-85-6; IIc, 81875-86-7.

Structure of an Unusual 1:2 Carbene–Methacrylonitrile Adduct. Chemical Evidence for Nitrile Ylide Formation

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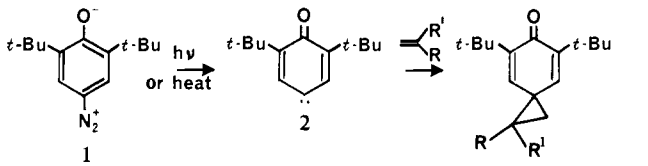
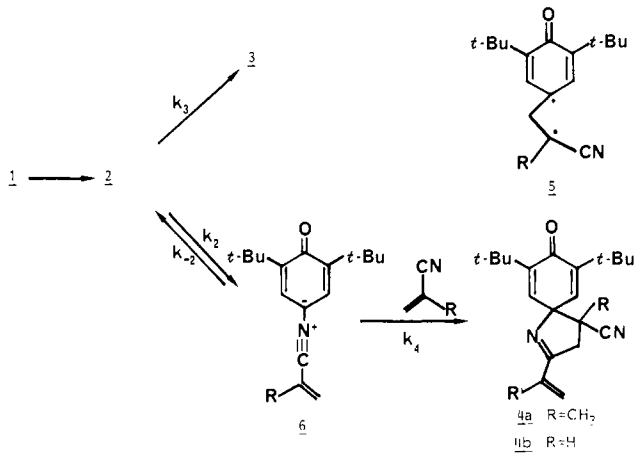
Current laser flash photolysis studies[1] of arylcarbenes in acetonitrile prompt us to describe the formation of unusual 1:2 cycloadducts between a carbene and unsaturated nitriles and to report evidence bearing on the reaction of a carbene with aliphatic nitriles.

It is well established from the work of the Nikiforov[2] and Pirkle[3] groups that thermal or photochemical decomposition of the *p*-diazo oxide **1** in the presence of substituted ethylenes leads to spiro-



dienones (**3**) postulated to arise by cycloaddition of the carbene **2** to the olefinic bond.[4] Similar chemistry has been observed by Schechter's group for 10-diazoanthrone.[5]

In connection with a synthetic problem, we have conducted the thermolysis of **1** in pure methacrylonitrile (MAN) as solvent (4% **1**, reflux 2 h). To our surprise, two nonaromatic crystalline adducts, mp 149–150 and 147–149 °C, were isolated by Si gel chromatography in yields of 38% and 48%, respectively. The minor product had a molecular formula $C_{18}H_{25}ON$,[6] IR maxima ($CHCl_3$) at 1620, 1656, and 2240 cm^{-1}, λ_{max} (hexane) 272 nm (ϵ 18 000),[7] and ^1H NMR and ^{13}C NMR spectra[8] uniquely consistent with the spirodienone structure **3a**. The major product (**4a**) had the molecular formula $C_{22}H_{30}ON_2$[9] corresponding to the



unexpected addition of *two MAN units to one of the carbene 2*. Photolysis (4% **1**, >350 nm, 15 °C, 8 h) of *p*-diazooxide **1** in pure MAN also led to the formation of both adducts **3a** and **4a** in an approximately 1:1 ratio. When the *p*-diazooxide **1** was thermolyzed in pure acrylonitrile (4% **1**, reflux 14 h), a $C_{17}H_{23}ON$ adduct (**3b**), mp 122–123 °C,[2] and a $C_{20}H_{26}ON_2$ adduct (**4b**), mp 119–120.5 °C, were formed in yields of 43% and 28%, respectively. The spectroscopic properties of the adducts **3b**[10] and **4b**[11] closely paralleled those of the MAN series.

Our initial hypothesis, that the 1:2 carbene–MAN adduct **4a** might be a secondary reaction product arising from the interception of a second MAN unit by a thermally generated 1,3-diradical[12] (**5**) derived from opening of the cyclopropane ring of adduct **3a**, was quickly disproved. Prolonged heating of adduct **3a** in refluxing MAN led simply to recovery of **3a** in excellent yield. Moreover, detailed spectrometric analysis of **4a** demonstrated that the incorporation of a second MAN unit did not entail addition to the C=C bond of that unit. Thus the 400-MHz ^1H NMR of adduct **4a** not only showed the characteristic β-enone protons of a cyclohexadienone unit (δ 6.14 (d, J = 3Hz, 1 H), 6.65 (d, J = 3Hz, 1 H)) but revealed an isolated CH_2 group with diastereotopic protons (δ 2.98, 3.03, 3.53, 3.58; AB system, J = 18 Hz, 2 H) as well as a saturated CH_3 (δ 1.33 (s, 3 H)), an allylic CH_3 (δ 2.10 (br s, 3 H)), and terminal methylene (δ 5.55 (br s, 1 H), 5.68 (br s, H)). These data, taken with IR maxima at 1650, 1667, and 2240 cm^{-1} and λ_{max} (CH_3OH) 232 nm (ϵ 29 700) indicated that the adduct **4a** was probably formed by an addition to the C=C of one MAN unit and to the C≡N of another. A crystal of **4a**, grown from hexane and selected for intensity and unit cell measurements employing an Enraf-Nonius CAD-4 automatic X-ray diffractometer, was shown to be monoclinic in the space group $P2_1/c$: a = 12.177 (9) Å, b = 14.553 (9) Å, c = 13.014 (8) Å, β = 111.38 (3)°, Z = 4. From a total of 4462 reflections collected, 1291 were classified as observed [$F_o^2 > 3(\sigma(F_o)^2)$]. MULTAN 79 was utilized to locate all non-hydrogen atoms. The hydrogen atoms were located from difference Fourier maps. Subsequent refinement converged in four cycles to give R = 7.9%.

The structure **4a** thus shown for the 1:2 carbene–MAN adduct required a new mechanistic rationale. Control studies showed that the yield and ratio of adducts **3a** and **4a** from **1** were essentially unaffected by O_2, p-$(OMe)_2C_6H_4$, m-$(NO_2)_2C_6H_4$, 5% $CHBr_3$,

(1) (a) Zupancic, J. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 5958; **1981**, *103*, 944. (b) Hadel, L. M.; Platz, M. S.; Senthilnathan, V. P.; Wrist, B. B.; Scaiano, J. C., submitted for publication. These workers find that the intersystem crossing rate of singlet 1-naphthylcarbene in CH_3CN is at least 5 times slower than in C_6H_6 and suggest the possible stabilization of the carbene in CH_3CN by reversible complexing with solvent to give a nitrile ylide. We are grateful to Professor Platz for communicating these results prior to publication.

(2) Nikiforov, G. A.; Sviridov, B. D.; Ershov, V. V. *Izvest. Akad. Nauk SSSR* **1968**, *3*, 558. This reference gives mp 118–119.5 °C for **3b**.

(3) Koser, G. F.; Pirkle, W. H. *J. Org. Chem.* **1967**, *32*, 1992. Pirkle, W. H.; Koser, G. F. *J. Am. Chem. Soc.* **1968**, *90*, 3598.

(4) Evidence for a ground-state triplet structure for carbene **2** has been discussed by Koser (Koser, G. F. *J. Org. Chem.* **1977**, *42*, 1474).

(5) Fleming, J. C.; Schechter, H. *J. Org. Chem.* **1969**, *34*, 3962.

(6) Found for **3a**: C, 79.63; H, 9.14; N, 5.00.

(7) This unusual λ_{max} is characteristic of such spiro[2,5]octa-3,6-diene-5-ones and has been ascribed to cyclopropane spiroconjugation. See, for example: Baird, R.; Winstein, S. *J. Am. Chem. Soc.* **1963**, *85*, 567.

(8) **3a**: ^1H NMR ($CDCl_3$) δ 1.23 (9 H, s), 1.27 (9 H, s), 1.59 (3 H, s), 1.70 (1 H, d, 5.4 Hz), 2.07 (1 H, d, 5.4 Hz), 6.12 (1 H, d, 3 Hz), 6.38 (1 H, d, 3 Hz); ^{13}C NMR ($CDCl_3$) δ 184.80, 151.74, 150.16, 139.72, 135.42, 120.91, 35.43, 35.13, 32.52, 30.58, 29.24 (corresponding to the $(CH_3)_6$ of *tert*-butyl groups) 22.69, 18.50.

(9) **4a**: found C, 78.07; H, 9.04; N, 8.27; ^{13}C NMR δ 185.47, 174.49, 150.10, 149.25, 138.39, 135.11, 123.89, 121.76, 76.63, 47.81, 47.20, 35.37, 35.23, 29.36, 29.24, 21.72, 19.11.

(10) **3b**: IR ($CHCl_3$) 1630, 1656, 2240 cm^{-1}; UV (hexane) λ_{max} 268 nm (ϵ 17 400); ^1H NMR ($CDCl_3$) δ 1.23 (9 H, s), 1.27 (9 H, s), 1.90 (2 H, m), 2.25 (1 H, dd, J = 9, 6 Hz), 5.85 (1 H, d, J = 3 Hz), 6.32 (1 H, d, J = 3 Hz).

(11) **4b**: IR ($CHCl_3$) 1650, 1668, 2240 cm^{-1}; UV (hexane) λ_{max} 229 nm (ϵ 30 000); ^1H NMR ($CDCl_3$) δ 1.26 (9 H, s), 1.28 (9 H, s), 3.25 (2 H, m), 3.45 (1 H, m), 5.84 (1 H, d, J = 17 Hz), 5.90 (1 H, d, J = 11 Hz), 6.30 (1 H, d, J = 3.6 Hz), 6.36 (1 H, d, J = 3.6 Hz), 6.71 (1 H, dd, J = 17, 11 Hz).

(12) The facile thermal and photochemical cis–trans isomerization of certain spiro[2,5]octa-3,6-dien-5-ones has been ascribed to the reversible formation and reclosure of such 1,3-diradical species. Pirkle, W. H.; Smith, S. G.; Koser, G. F. *J. Am. Chem. Soc.* **1969**, *91*, 1580.

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