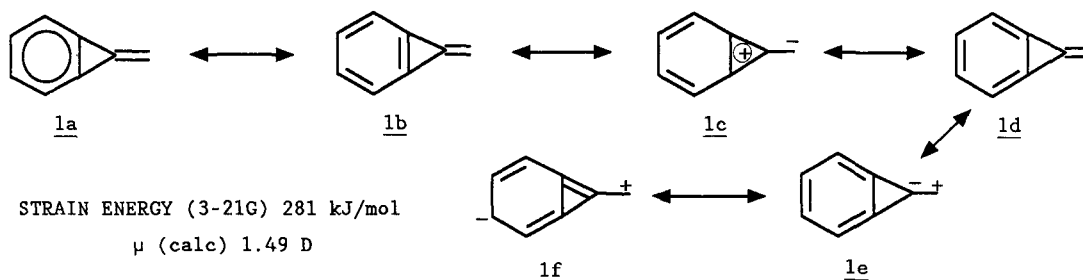# Alkylidenecycloproparenes: strained and polar aromatics

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Abstract - The alkylidenecycloproparenes are strained (~281 kJmol⁻¹) and polar (μ 0.5-3.0 D) compounds; the magnitude and direction of the permanent dipole depends upon the substitution pattern present. The dimethylaminophenyl derivative **17** fluoresces strongly (Y_F 0.96). Flash vacuum pyrolysis of **12** and **19** leads to polycyclic aromatics by way of three-membered ring cleavage and insertion. Metal atom insertion and ring expansion occurs upon reaction with rhodium and platinum complexes.

The discovery that diarylmethylenecycloproparenes, cf. **1**, are surprisingly stable coloured crystalline solids is recent and is in marked contrast to their 1-oxo analogues, the benzocyclopropenones (refs. 1-3). Stable derivatives of methylenecyclopropene have been known for twenty-five years (ref. 4) but the parent hydrocarbon has only recently been reported (ref. 5) and is unstable at temperatures above -75°C. Similarly, the smallest parent radialene, trimethylenecyclopropane, polymerizes above 0°C (ref. 6). The alkylidenecycloproparenes, eg. **1**, combine into one molecule the features associated with both of these hydrocarbons. Thus they may be regarded as a cycloproparene **1a**, a

STRAIN ENERGY (3-21G) 281 kJ/mol

μ (calc) 1.49 D

benzannulated methylenecyclopropene **1b**, a benzannulated triafulvene **1b-1c**, an unusual radialene **1d**, and an inversely polarized fulvene **1e-1f** all in one.

The most general route to the alkylidenecycloproparenes couples the acidity of the benzylic protons of the parent cycloproparene hydrocarbon with Peterson olefination (Scheme 1) and with suitable modification the sequence is applicable to the preparation of the corresponding cyclopropa[*b*]naphthalene homologues (refs. 2,3). Because base is necessary for carbanion formation, carbonyl compounds which carry an α-hydrogen frequently fail to react presumably

Scheme 1
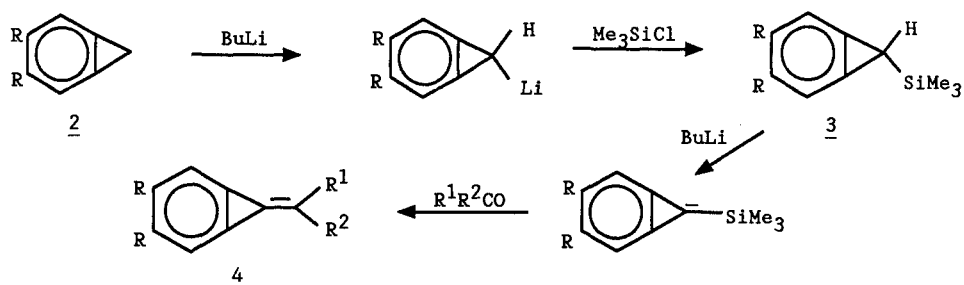
because of enolate ion formation. Furthermore the methodology has yet to yield parent species, eg. **1**. The widest application of the route is to derivatives which carry aryl- or diarylmethylene substitution and a good range of such compounds as stable, colored crystalline solids now exists (refs. 2,3,7,8).

Apart from these fulvenes the fluorenylidene **5** and dibenzocycloheptatrienylidene **6** derivatives are available (ref. 7). The compounds have measurable permanent dipole moments (**5**: 2.6 D; **6**: 1.2 D) which are in excellent agreement with the values calculated for the parent systems **7** (3.28 D) and **8**

R = H μ = 2.6 D   R = H μ = 1.2 D   μ (calc) 3.28 D   μ (calc) 1.12 D

5   **6**   **7**   **8**
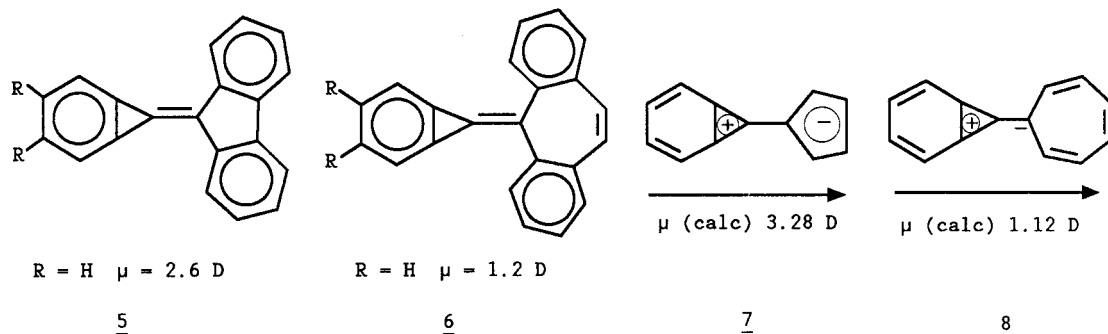
(1.12 D) respectively (ref. 9). Especially noteworthy is the fact that the direction of the calculated dipole in **1**, **7** and **8** is the *same*. It follows, therefore, that the cycloheptatrienyl moiety is not a strong enough electron donor to reverse the polarity to a 6π7C tropylium cation/benzylic anion contributor, cf. **1e-f**. The same direction of polarity (viz. **1c**) is presumed to be present in the dibenzo homologue **6** and is supported by the outcome of electrophilic additions which effect protonation at C1′, the negative end of the dipole, to deliver (ultimately) ring cleaved and ring expanded products (Scheme 2).

The preparation of alkylidenecyclopropiarenes with effective electron donating substituents attached to the exocyclic double bond has now been accomplished and the compounds have significant permanent dipoles (Chart 1). Notable amongst these compounds is the dinitro derivative **15**. Because of the sensitivity of 4,4′-dinitrobenzophenone to t-butoxide the preparation of **15** from disilylcyclopropa[b]naphthalene (ref. 2) requires a modified procedure. The reaction is effected in acetonitrile by employing an excess of insoluble potassium fluoride. The anion is transferred by a catalytic quantity (25 mol %) of tetrabutylammonium fluoride and dinitro **15** is obtained in 88% yield; the reaction fails for the cyclopropabenzene equivalent. Unfortunately compound **15**, which clearly
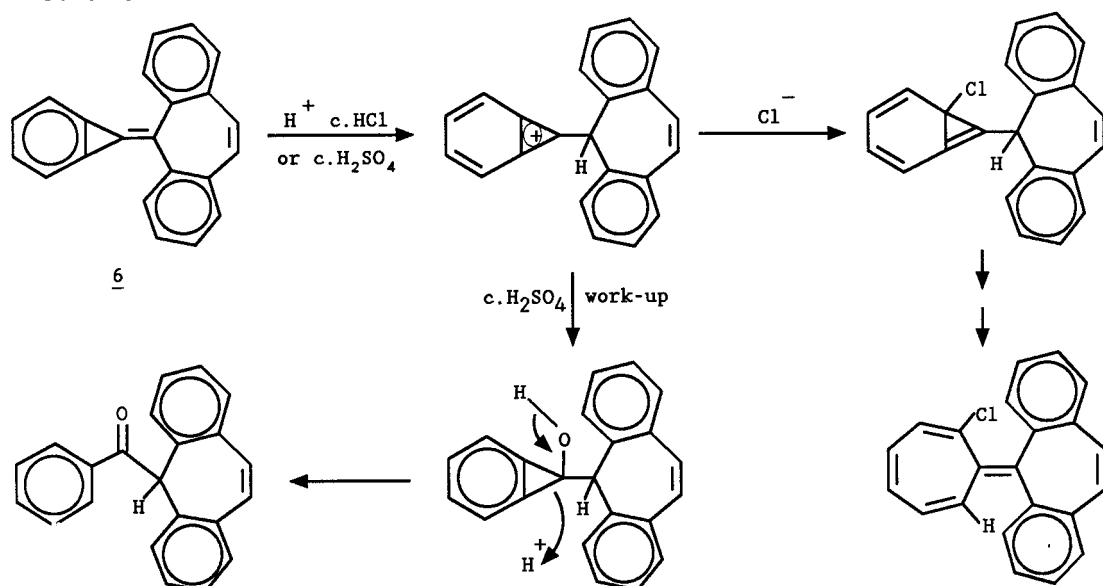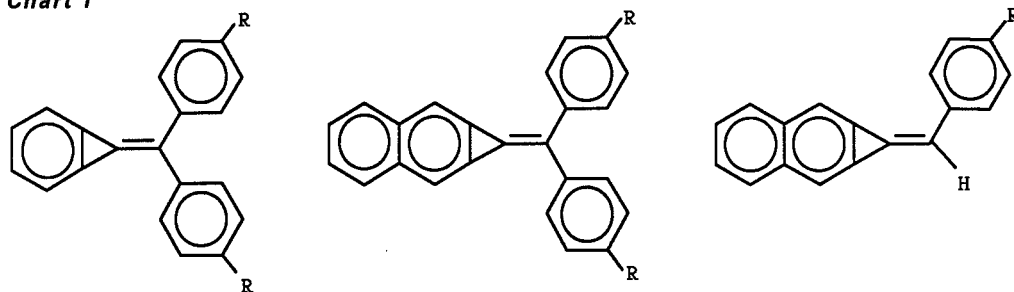
Scheme 2

Chart 1

μ = 1.0 D	9	R = H	12	μ = 0.4 D	16	R = OMe	μ = 1.4 D
1.9	10	R = OMe	13	2.4	17	R = NMe$_2$	μ = 1.8 D
2.2	11	R = NMe$_2$	14	3.0			
		R = NO$_2$	15	insoluble			

should have polarity in the opposite direction to that in **14**, is insufficiently soluble in benzene to allow for capacitance measurements and dipole moment calculation. However the polar natures of e.g. **5** and **11** establish that the cycloproparenyl moiety is ambiphilic (ref. 8). The charge separation, **1c** vs **1e-f**, is dictated therefore by the nature of the substituents attached to the exocyclic double bond. The polarity of the compounds is reflected in the intensity of the characteristic (ref. 3) infrared stretching vibration at ~1770 cm^{-1} (Fig. 1). This band results from a combination of the three-membered ring endo- and exocyclic double bond stretches; as the polarity increases the intensity decreases. Notable is the fact that removal of the non-bonding electron pairs by quaternization of the nitrogen atoms of **11** (**14** or **17**) restores the combination band. A similar effect occurs for the long wavelength ultraviolet absorption maxima (ref. 8).

· During the isolation of the dimethylamino substituted compounds, and especially **17**, it became obvious that the extended conjugation and the nature of the substituents provided a notable lumophore. Emission spectroscopy has established that compounds **10**, **11**, **13**, **14**, **16** and **17** are markedly more fluorescent than their parents. The absolute quantum yields (Y_F) for **14** and **17** in cyclohexane are 0.81 and 0.96 respectively (refs. 10,11). Fig. 2 depicts the absorption-emission characteristics of **17** which has a pronounced Stokes shift and high Y_F in dimethylformamide (dmf). The compound lases very effectively over a wide turning range (≥ 100 nm) but the limits of this action have yet to be set (refs. 10,11). The bisdimethylamino analogue **14** is markedly less stable in dmf but it too is strongly fluorescent with excellent lasing characteristics. Polarization spectroscopy has shown that phosphorescence is not involved and suggest that the high capacity these compounds have for fluorescence is most likely due to a twisted internal charge transfer (TICT) state (ref. 12). The donation of an electron from the nitrogen non-bonding electron pair to the cycloproparenyl moiety is not at all untoward. The parent compounds **9** and **12** are known to undergo electrochemical oxidation and reduction to a cation radical and anion radical respectively, which have some 70% of the charge resident in the diarylmethylene moiety (ref. 13). We suggest therefore that S_0-S_1 excitation is followed by a twisting of, and electron transfer from, the nitrogen atom to give an
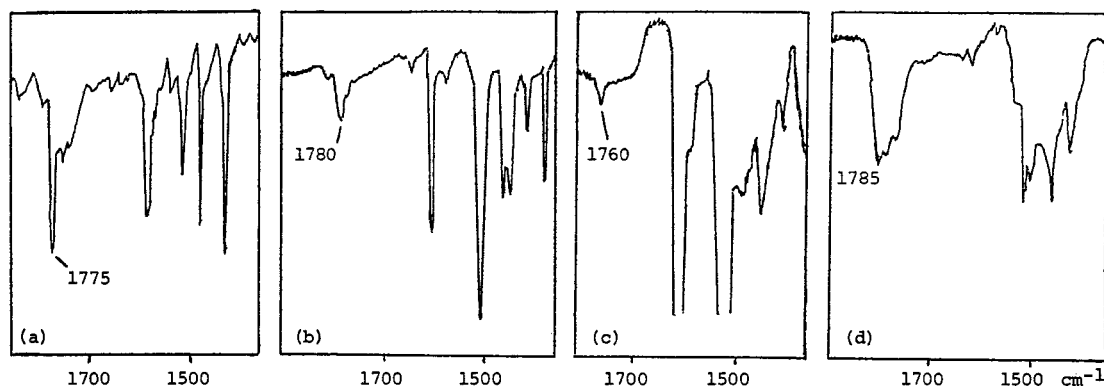

Fig. 1. Partial infrared spectra (KBr) of (a) **9**, (b) **10**, (c) **11** and (d) the bis(trimethylammonio) derivative of **11**.
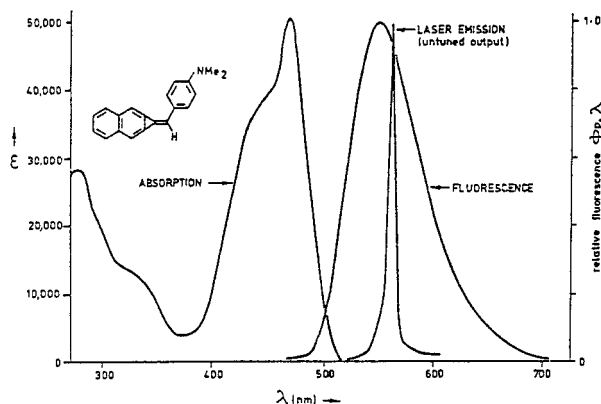
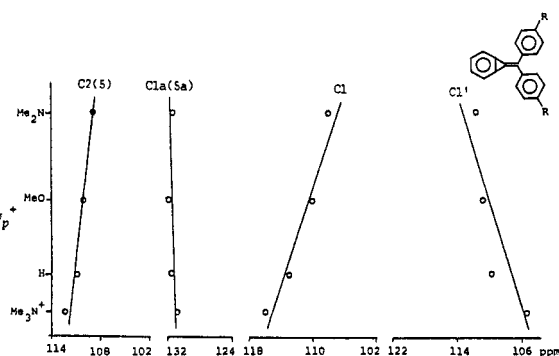Fig. 2. Absorption-emission spectra of **17** in dimethylformamide.

Fig. 3. [13]C Chemical shift correlations for the diarylmethylenecyclopropabenzenes.

excited TICT singlet state with the radical centre delocalized into the cycloproparenyl sub-structure. Fluorescence likely leads to the TICT ground state before collapse to the molecular ground state S_o.

It is now established that the mesomeric contribution of a functional group and the ^{13}C chemical shift of an affected carbon can be correlated by linear free energy relationships. Specifically, correlation with the Hammett σ_p^+ constant, which has a 66% resonance contribution, provides an appropriate measure of changes in π-electron density over as many as eight bonds (refs. 14,15). The chemical shifts of all the cyclopropabenzenyl as well as the olefinic C1'atom correlate well as shown in Fig. 3 for C1, C1a(5a) and C2(5) and C1'; equally favourable plots for the naphthalene series are obtained. There is a systematic high field shift of C1, C2(5) and C3(4) and a systematic low field shift of C1' and C1a(5) as the electron donating ability of the remote *para*-aryl substituent increases. The relative sensitivity of the ring carbon atoms and the σ_p^+ correlations are fully compatible with increased electron density at C1, C2 and C4 (cf. **1e-f**) and reduced density at C1' and C1a as expected from mesomerism of the remote substituent.

Crystallographic parameters have been obtained for a number of the compounds and Table 1 lists data for the three-membered ring of **5** and **14** together with those for their parent precursors. The effect of converting C1 from sp[3] to sp[2] is to widen the C1a-1-5a angle (β) by ~4° while at the same

TABLE 1. Selected Structural Parameters[a]

Compound	a	b	c	α	β	γ	exo[b]
R[1]=R[2]=H	1.334	1.498	1.367	64.6	52.8	171.7	–
R[1]=H; R[2]R[2]= fluorenyl	1.377	1.441	1.385	61.5	57.1	174.8	1.338
R[1]R[1]=benzo; R[2]=H	1.375	1.503	1.355	62.8	54.4	172.0	–
R[1]R[1]=benzo R[2]R[2]= =C(p-C₆H₄NMe₂)₂	1.399	1.440	1.352	60.9	58.1	174.5	1.346

[a]Bond lengths in Angstrom units (±0.003) and angles in degrees
(±0.2). Data collected by Dr. R. Boese, University of Essen.
[b]Exocyclic double bond length.

time the bridge bond **a** is lengthened by 0.02-0.04 Å; the lateral σ-bonds are markedly shortened (~0.06 Å). The fusion angle γ is widened almost to linearity while α is reduced by 2-3°, but the exocyclic double bond length is essentially unaffected by the changes. It has been noted previously that π-electronic effects are not always mirrored in the geometry of the system (ref. 9). What is obvious here is that the changes recorded reflect the planarization of C1.

Recent chemical studies have encompassed the behaviour of the compounds upon flash vacuum pyrolysis. Cyclopropabenzene undergoes ring contraction to cyclopentadienylidenallene (ref. 16) perhaps as shown below in which Wolf rearrangement of the ring opened carbene is involved. Applied to **1** one might anticipate the formation of the corresponding propatriene:
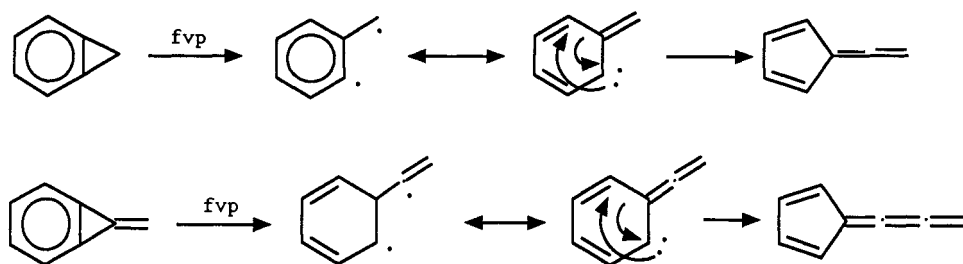
However, the derivatives **12** and **18** yield complex product mixtures from which only dibenzoacephenanthrylenes (Scheme 3) have been isolated thus far. It is clear that the arylmethylene substitution markedly influences the course of reaction by providing suitably located centres for ring expansion. Diphenyl **9** must undergo dehydrogenation but it is not known whether this precedes the ring closure to give the six-membered ring.

Scheme 3
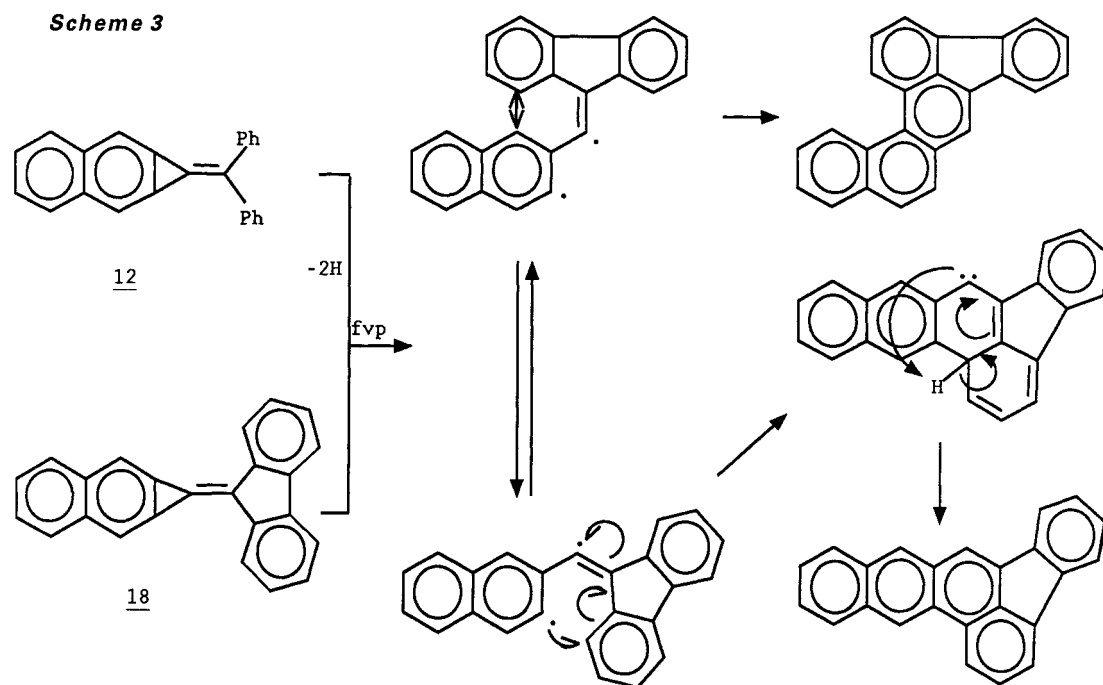
The extended conjugation in **1** has prompted an investigation of the behaviour of the derivatives with organometallic reagents (ref. 17). With rhodium the outcome depends upon the nature of the complex. Thus Wilkinson's catalyst leads to carbonyl insertion and the ring expanded metallocycle

9 R = H or
12 RR = benzo

19 minor

21 major
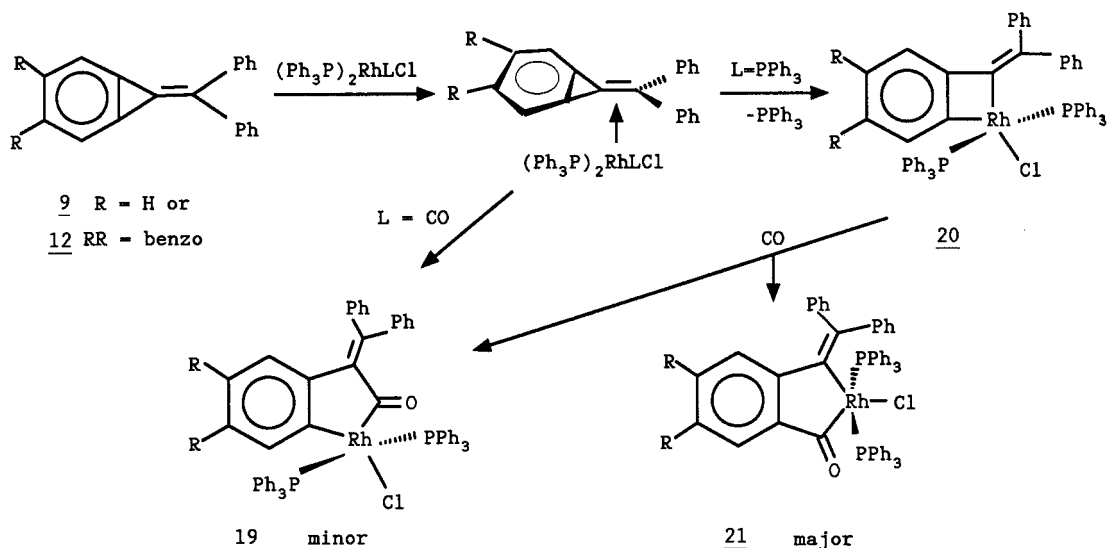
19 (X-ray structure) is obtained in high yield. We presume that π-complexation with the exocyclic alkene is followed by ring cleavage and insertion of the metal at the most electronegative centre. By comparison the tris(triphenylphosphine) complex ejects a ligand to give the rhodiacyclobutarene **20**. Reaction of **20** with carbon monoxide provides regioselective insertion and the conjugated aryl ketone **21** is obtained by cleavage of the weakest rhodium-carbon bond. Platinum complexes likewise afford platinacyclobutarenes. The results of these and other studies involving these novel hydrocarbons will form the basis of future publications.

Acknowledgement

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