Synthesis and properties of sterically congested cyclopentadienes and their transition metal complexes

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Abstract:

The synthesis of 1,3-dialkyl substituted cyclopentadienes, C_5H_4RR', Cp′H (Va-g) (where R and R′ are tert-butyl, isopropyl, neo-pentyl, cyclohexyl, or 1-methylcyclohexyl) is reported. These are synthesized by the nucleophilic addition of methyl or hydride anions to the corresponding 2-alkyl-6,6-dialkylfulvenes (IIIa-f) followed by hydrolysis. These substituted 1,3-cyclopentadienes have been converted to organometallic derivatives such as $[Cp'Fe(CO)_2]_2$, $[Cp'M(CO)_3Me]$ (M = Mo or W) and Cp'_2Fe. The spectroscopic and electrochemical properties of selected complexes have been investigated to probe the steric and electronic properties of the substituted cyclopentadienyl ligands.

Article:

1. Introduction

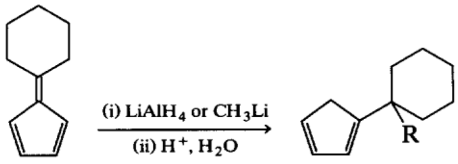
Substituted cyclopentadienyl complexes differ greatly in reactivity, structural features and physical properties from their unsubstituted counterparts [1]. Changes in both electronic and steric factors contribute to these differences [2]. The pentamethylcyclopentadienyl ligand, Cp*H (I) is the most notable example of a substituted cyclopentadiene and has been utilized extensively. For example, Maitlis *et al*. have shown that $[CpRhCl_2]_n$ is polymeric, insoluble in most organic solvents, and the Cp-Rh bond is readily cleaved by various reagents. In stark contrast, $[Cp^*RhCl_2]_2$, is dimeric, soluble in organic solvents, and the Cp*-Rh bond withstands acidic, basic, oxidizing and reducing conditions [3].

The variety and number of substituted cyclopentadienes available has been limited until recently. The methyl substituted series has been extensively studied, as well as several monoalkylsubstituted derivatives [4]. Recent efforts have been directed toward the study of transition metal cyclopentadienyl complexes containing chiral and functionalized substituents [5]. Several workers have investigated the chemistry of tetraphenyl [6], pentaphenyl [7], and pentabenzyl-cyclopentadienyl [8] organometallic compounds. Sitzmann and Hanusa have recently reported the elegant syntheses of highly substituted cyclopentadienes [9,10].

We report here on the regioselective synthesis of sterically congested 1,3-disubstituted cyclopentadienes and the synthesis of selected transition metal derivatives. Preliminary results of this work have recently been reported [11,12].

1.1. Synthesis of monosubstituted 1,3-cyclopentadienes

Among the methods of cyclopentadiene synthesis, the addition of nucleophiles to fulvenes is one of the most useful [13]. The excellent fulvene synthesis recently developed by Little *et al.* [14] has made this route very attractive. We have utilized this reaction to make the monoalkylsubstituted cyclopentadienes needed as precursors for our synthesis of dialkylfulvenes and substituted cyclopentadienes. The addition of methyl or hydride anions to 6,6-pentamethylenefulvene leads to good yields of cyclohexyl-1,3-cyclopentadiene (IIa) or (1′-methylcyclohexyl)-1,3-cyclopentadiene (IIb)**, after hydrolysis of the intermediate cyclopentadienyl anions (eqn. (1)). A similar route to IIb has recently been reported by Collins *et al.* [15].



(1)

IIa: R = H
IIb: R = Me

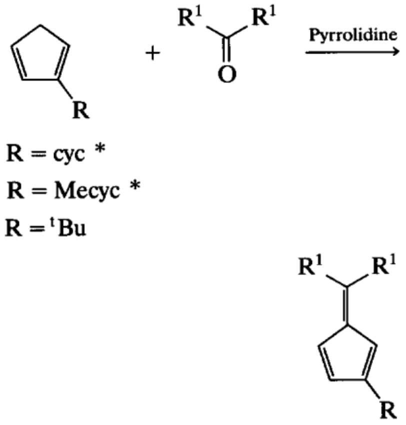
(1-Methylcyclohexyl)-1,3-cyclopentadiene was identified by its ^{1}H NMR spectrum and microanalysis of its tetracyanoethylene Diels—Alder adduct. The synthesis of tert-butyl-1,3-cyclopentadiene (IIc) was accomplished by the addition of methyllithium to 6,6-dimethylfulvene [13].

1.2. Synthesis of 2-substituted fulvenes

In order to extend this route to the formation of 1,3-dialkylcyclopentadienes, we have synthesized a series of 2-alkyl-6,6-dialkylfulvenes. Preliminary results of these studies have been reported [11].

The pyrollidine-catalyzed condensation of the substituted cyclopentadienes, IIa-c, with acetone or cyclohexanone yielded 2-substituted-6,6-dimethylfulvenes, IIIa-c, or 2-substituted-6,6-pentamethylenefulvenes, IIId-f.

In addition, *E*- and *Z*-2-t-butyl-6-t-butylfulvene (IIIg) was synthesized from IIc and trimethylacetaldehyde using a modification of the published method [16]. The synthesis of Inc was also published during our studies [17].



IIa: R = cyc *
IIb: R = Mecyc *
IIc: R = ^{t}Bu

(2)

IIIa: R^1 = Me; R = cyc *
IIIb: R^1 = Me; R = Mecyc *
IIIc: R^1 = Me; R = ^{t}Bu
IIId: R^1, R^1; = $[CH_2]_5$; R = cyc *
IIIe: R^1, R^1 = $[CH_2]_5$; R = Mecyc *
IIIf: R^1, R^1 = $[CH_2]_5$; R = ^{t}Bu

The regiospecificity of the fulvene formation from substituted cyclopentadienes was confirmed by ^{1}H and ^{13}C NMR spectra Tables 1 and 2 and by the formation of Diels—Alder adducts with tetracyanoethylene.

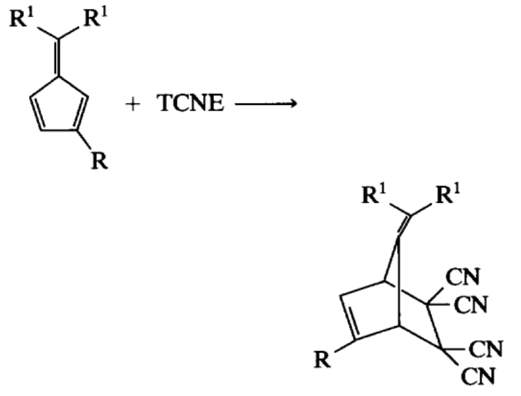
TABLE 1. 500 MHz ^{1}H NMR spectra of 2-substituted-6,6-dialkylfulvenes [a]

Fulvene	H_1 [b]	H_3 [b]	H_4 [b]	$J_{1,3}$ [c]	$J_{3,4}$ [c]	$J_{1,4}$ [c]
IIIa	6.12	6.37	6.46	1.35	5.33	2.00
IIIb	6.18	6.46	6.49	1.81	5.46	2.19
IIIc	6.25	6.58	6.60	1.57	5.43	2.21
IIId	6.16	6.40	6.50	1.52	5.46	2.21
IIIe	6.22	6.49	6.53	1.85	5.41	2.17
IIIf	6.17	6.49	6.54	–	–	–

[a] Spectra were recorded at 500 MHz using TMS as a standard reference. [b] δ (ppm). [c] *J* (Hz).

The shielding effects and coupling constants for IIIa-f (Table 1) were similar to those reported by Albeit and Roth [16] for *E*- and *Z*-t-butyl-6-t-butylfulvene. This allows assignment of H_1, the proton attached to C_1, as the upfield resonance, H_3, the proton attached to C_3, as the intermediate peak and H_4, the proton attached to C_4, and the most highly deshielded proton. Coupling constants also confirmed these assignments as they were quite similar to those reported for unsubstituted fulvenes reported by Neuenschwander *et al.* [18].

The structures of the substituted fulvenes were also confirmed by the formation of Diels—Alder adducts with tetracyanoethylene (eqn. (3)).



(3)

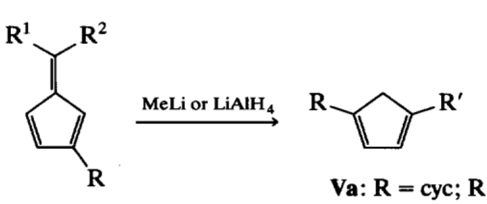
IVa: $R^1 = Me$; R = cyc
IVb: $R^1 = Me$; R = Mecyc
IVd: $R^1, R^1 = [CH_2]_5$; R = cyc
IVe: $R^1, R^1 = [CH_2]_5$; R = Mecyc
IVf: $R^1, R^1 = [CH_2]_5$; R = ^{t}Bu

TABLE 2. ^{13}C NMR spectra of 2-substituted-6,6-dialkylfulvenes [a]

Fulvene	C_1	C_2	C_3	C_4	C_5	C_6
IIIa	112.9	146.5	131.5	121.1	142.2	152.6
IIIb	113.1	146.3	130.5	121.2	142.2	155.7
IIIc	111.7	146.8	130.5	121.3	141.9	156.5
IIId	112.4	152.5	131.6	120.5	139.1	154.7
IIIe	112.6	154.3	130.6	120.6	139.3	155.7
IIIf	111.4	154.6	130.7	120.8	139.3	156.7

[a] δ (ppm); spectra were recorded at 50.3 MHz using $CDCl_3$ as an internal reference.

No adduct was prepared from IIIc as it has previously been synthesized. All the adducts, IV, were identified by their ^1H NMR spectra, which showed the presence of only one olefinic proton, and by satisfactory microanalysis.



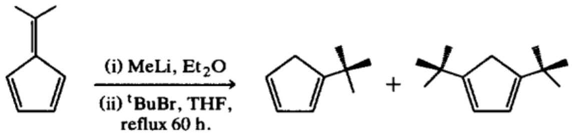
(4)

Va: R = cyc; R′ = ^{t}Bu
Vb: R = cyc; R′ = ^{i}Pr
Vc: R = ^{t}Bu; R′ = ^{i}Pr
Vd: R = R′ = cyc
Ve: R = R′ = Mecyc
Vf: R = ^{t}Bu; R′ = cyc
Vg: R = ^{t}Bu; R′ = neo-pent

1.3. 1,3-Dialkylsubstituted cyclopentadienes

The reaction of methylithium or lithium aluminum hydride with the substituted fulvenes IIIa-g, followed by hydrolysis leads to 1,3-dialkylcyclopentadienes in good yield, as mixtures of double bond isomers (eqn. (4)). The 1,3-disubstituted cyclopentadienes synthesized are included in Table 3, together with their yields.

In addition, a mixture of t-butyl-1,3-cyclopentadiene and 1,3-di-t-butylcyclopentadiene was synthesized from the t-butylcyclopentadiene anion. This was formed *in situ* from 6,6-dimethylfulvene and methyllithium and then reacted with t-butylbromide by refluxing in a mixture of diethylether and THF for 60 h. The mono-and di-t-butylcyclopentadienes were easily separated by fractional vacuum distillation in 14% and 52% yield respectively (eqn. (5)).



(5)

Di-1,3-t-butylcyclopentadiene has previously been synthesized using a two-step route by Neuenschwander [19]. More recently, Casserly has reported a one-step process using phase transfer catalysis [20]. A similar reaction between the cyclohexylcyclopentadienide anion, from 6,6-pentamethylenefulvene and lithium aluminum hydride, and cyclohexylbromide was used to make a mixture of cyclohexyl-1,3-cyclopentadiene (IIa) (10% yield) and 1,3-dicyclohexylcyclopentadiene (Vd) (35% yield).

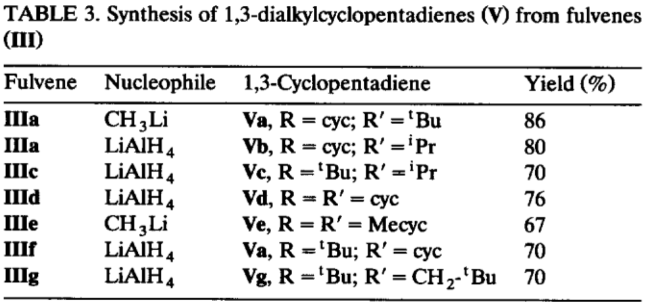


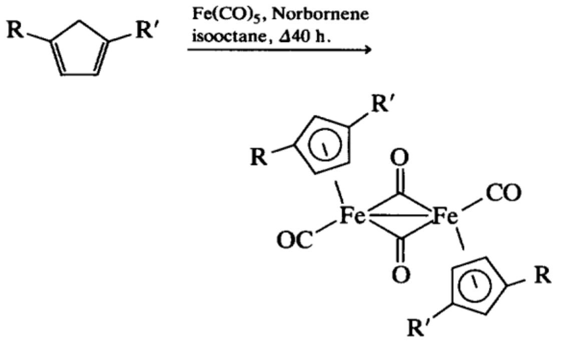
TABLE 3. Synthesis of 1,3-dialkylcyclopentadienes (**V**) from fulvenes (**III**)

Fulvene	Nucleophile	1,3-Cyclopentadiene	Yield (%)
IIIa	CH_3Li	**Va**, R = cyc; R′ = ^{t}Bu	86
IIIa	$LiAlH_4$	**Vb**, R = cyc; R′ = ^{i}Pr	80
IIIc	$LiAlH_4$	**Vc**, R = ^{t}Bu; R′ = ^{i}Pr	70
IIId	$LiAlH_4$	**Vd**, R = R′ = cyc	76
IIIe	CH_3Li	**Ve**, R = R′ = Mecyc	67
IIIf	$LiAlH_4$	**Va**, R = ^{t}Bu; R′ = cyc	70
IIIg	$LiAlH_4$	**Vg**, R = ^{t}Bu; R′ = CH_2-^{t}Bu	70

2. Synthesis and spectroscopic of transition metal complexes

2.1. Substituted cyclopentadienyliron dicarbonyl dimers

A series of substituted cyclopentadienyliron dicarbonyl dimers, VIa-c and g, were synthesized from dialkyl-1,3-cyclopentadienes, Va-c and g, and iron pentacarbonyl using the method of Paquette *et al.* [21] (eqn. (6)).

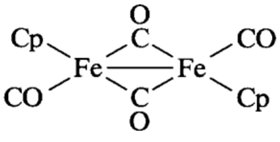


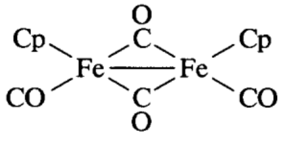
(6)

Va, VIa: R = cyc; R′ = t-butyl
Vb, VIb: R = cyc; R′ = i-propyl
Vc, VIc: R = t-butyl; R′ = i-propyl
Vg, VIg: R = R′ = t-butyl
Vh, VIh: R = R′ = $SiMe_3$
Vi, VIi: R = t-butyl; R′ = neo-pent

For comparison purposes, the literature complexes Vg (R = R′ = ‘Bu) and Vh (R = R′ = $SiMe_3$) were synthesized by refluxing the cyclopentadienes with $Fe_2(CO)_9$ in hexane for 12 h [22,23]. The new compounds, VIa—c and g, were characterized by their ^1H NMR, IR spectra and microanalysis.

Cyclopentadienyliron dicarbonyl dimer, VII, has been shown to exist as a mixture *cis,* VIII, *trans,* IX, and unbridged, X, isomers in solution by ^1H NMR, ^{13}C NMR, and IR spectroscopies [24].


(VIII)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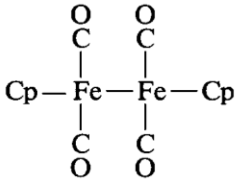

(X)

The relative amounts of isomers are solvent dependent and interconversion occurs quite readily. The infrared spectra of VIg and VIh have been recorded in various solvents and the relative amounts of *cis*- and *trans*-isomers have been calculated by the method of Manning [24] (Table 4). Both compounds follow the general trend of increased amounts of *cis*-isomer as the solvent polarity increased, as was found for the unsubstituted dimer, VII.

In addition the infrared spectra of VIa—VIc were recorded in hexane solution as the *trans*-isomer predominates (Table 5). The prediction is that sterically more demanding ligands would afford a higher percentage *trans*-isomer, for example pentamethylcyclopentadienyliron dicarbonyl dimer, XI, exists predominantly as the *trans*-isomer [25]. Unexpectedly, the percentage of trans-isomer for complexes VIa—VIc with the more bulky cyclopentadienyl ligands is decreased relative to VII. Manning *et al.* [26] observed a similar trend in a series of monosubstituted cyclopentadienyl complexes and attributed this phenomenon to increased solubility of the *cis*-isomer in nonpolar solvents due to a reduction of the dipole moment. This increased stability is much greater than the steric interactions brought about by the substituents. Disubstitution, however, lowers the percentage *trans*-isomer more than expected.

TABLE 4. Solution infrared spectra of **VIg** and **VIh** [a]

Complex	Hexane	Dichloromethane	Acetonitrile
VIg	33	25	18
VIh	42	28	22
VII	64	39	18

[a] Percent *trans*-isomer; balance *cis*-isomer.

TABLE 5. Isomeric ratios of cyclopentadienyliron dicarbonyl dimers in hexane solution [a]

Complex	% *Trans*	% *Cis*
VIa	42	58
VIb	60	40
VIc	40	60
VIg	33	67
VIh	42	58
VIi	41	59
VII [b]	64	36
XI [c]	100	0

[a] Spectra were recorded in hexane. [b] Ref. 24. [c] Ref. 25.

Complexes VIg and VIh possess similar steric bulk, although they are different electronically. A lowering of the percentage of *trans*-isomer compared to the unsubstituted complex, VII, was observed for both complexes. However, the percentage of *trans*-isomer for VIg and VIh were quite similar which suggests that electronic effects play a minor role in their solution structures.

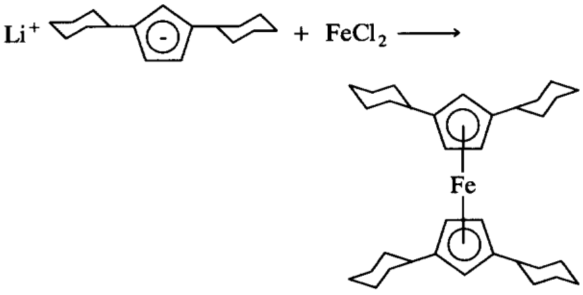
Calculations have shown that these effects are probably not due to distortions in the Fe-Fe-CO bond angle of the *cis*-isomer [27]. A 20° increase or decrease in the Fe-Fe-CO bond angle (97°) as determined from crystallographic data for VIII affords less than 1% change in the relative percentage of *trans*-isomer. Changes in geometry are therefore most likely not responsible for these unexpected results.

The ^1H NMR spectra of VIa—h exhibit two or three resonances for the cyclopentadienyl ring protons, separated by as much as 2 ppm. The spectra demonstrated no temperature dependence upon heating the complexes to 50°C. The distribution of isomeric forms *(i.e.* analogs of VIII, IX and X) of the complexes would be expected to change with temperature with associated spectral changes. Similar behavior has been observed previously for related systems and the effects were attributed to changes in the metal-cyclopentadienyl cone angle and anisotropy [28]. Coville has recently carried out an elegant study of the steric effects associated with cyclopentadienyl metal complexes and their association with NMR spectroscopic properties [29]. It has been suggested that the bridging carbonyl provides an unsymmetrical shielding effect due to hindered rotation of the cyclopentadienyl ligand.

The proton NMR spectra of these complexes also provides some insights into their solution structures. For example, complex VId exhibits two doublets for the isopropyl group. This indicates that the group is rotated so that one methyl group is toward the metal and the other methyl group is above the plane of the cyclopentadienyl ring.

2.2. Synthesis and properties of tetrakis-1,1’,3,3’-cyclohexylferrocene (XII)

Tetrakis-1,1′,3,3′-cyclohexyl ferrocene (XII) was prepared from lithium bis-1,3-cyclohexylcyclopentadienide and $FeCl_2$ by standard methods (eqn. (7)).



(7)

(XII)

Cyclic voltammetry of substituted terrocenes has yielded useful information about the electronic properties of substituted cyclopentadienyl ligand. A useful measure of these electronic effects is $\Delta E^\circ_{1/2}$, defined as the difference between $E^\circ_{1/2}$ for the substituted ferrocene and $E^\circ_{1/2}$ for ferrocene. The value of $\Delta E^\circ_{1/2}$ for XII is determined to be -0.235 V in acetonitrile relative to the standard calomel electrode. This indicates a more facile oxidation due to the electron donating cyclohexyl substituents. The value of $\Delta E^\circ_{1/2}$ is in good agreement with that of other tetrakisalkyl substituted ferrocenes, for example, 1,1′3,3′-tetrakis-t-butylferrocene has a value of -0.239 V for $\Delta E^\circ_{1/2}$ [30]. A value for the Hammett σ_p constant for the cyclohexyl substituent may be estimated using eqn. (8) [31] where $\Delta E^\circ_{1/2}$(subs) represents the value of $\Delta E^\circ_{1/2}$ per substituent.

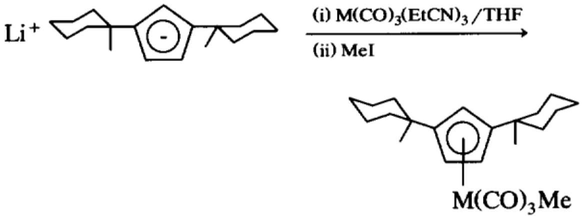
$$\Delta E^\circ_{1/2} = 0.464\sigma_p + 0.18\ \mathrm{V} \qquad (8)$$

The value obtained this way, cr(cyclohexyl) = — 0.17, is in good agreement with the literature value of u_p = — 0.22 [32].

The 500 MHz ^1H NMR spectrum of XII at room temperature indicated a singlet at 3.89 ppm for the cyclopentadienyl proton resonances. At -13°C the resonance began to split and at -83°C two distinct resonances appeared at 3.98 and 3.94 ppm. Unfortunately, the coalescence temperature could not be determined.

2.3. Synthesis and properties of bis-1,3-(1-methylcyclohexyl)cyclopentadienyl tricarbonylmethyl molybdenum (XIII) and tungsten (XIV)

The reaction of lithium bis-1,3-(1-methylcyclohexyl) cyclopentadienide with trispropionitriletricarbonylmolybdenum or tungsten in refluxing THF followed by reaction with iodomethane provides XIII or XIV (eqn. (9)). Preliminary details of our studies on XIV have been published [12].



(9)

XIII: M = Mo
XIV: M = W

The proton NMR spectrum of XIII in $CDCl_3$ indicates a single cyclopentadienyl resonance at 5.04 ppm for the three protons. The cyclopentadienyl protons are somewhat resolved in toluene-d_8 as they appear as a triplet at δ 4.91 ppm and a doublet at δ 4.72 ppm corresponding to one and two protons, respectively. The molybdenum analog, XI, was synthesized using a similar method and exhibited similar chemical and spectroscopic properties.

3. Experimental

3.1. General

All manipulations of moisture and air sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk and vacuum line techniques.

Tetrahydrofuran (THF), hexane and diethyl ether were pre-dried over sodium or powdered potassium hydroxide and freshly distilled from sodium benzophenone ketyl. Pyrrolidine was dried over activated molecular sieves and distilled and stored under nitrogen.

^1H NMR were recorded on Varian 60 MHz EM-360, Varian VXR 200 MHz, or the Yale 490 MHz spectrometers. ^{13}C NMR were recorded on a Bruker WM250. Infrared spectra were recorded on a Perkin Elmer 1320 spectrometer. GC-mass spectra were recorded on a Hewlett-Packard 5970 instrument. Ultraviolet-visible spectra were recorded on a Varian DMS 100S spectrophotometer using HPLC grade hexane. The purity of all volatile materials was confirmed using a Varian 3300 GC with a thermal conductivity detector using a 6ft. 5% OV 101 Chromasorb column. Cyclic voltammetry was carried out with a Cypress Systems CS 1087 Electrochemical Analyzer using a platinum bead working electrode, SCE reference electrode, tetraethylammonium perchlorate (TEAP) as the supporting electrolyte, and acetonitrile as the solvent.

Microanalyses were carried out by Desert Analytics, Tucson, Arizona. High resolution mass spectra were carried by the Midwest Center for Mass Spectrometric Analysis, Lincoln, Nebraska.

3.2. Syntheses

1-Cyclohexylcyclopenta-1,3-diene (IIa). A solution of 6,6-pentamethylenefulvene (10.0 g, 68.4 mmol) in diethyl ether (25 ml) was added to lithium aluminum hydride (2.70 g, 73.0 mol) in diethyl ether (200 ml) and the mixture was stirred for 0.5 h. The reaction mixture was quenched with water, then 10% HCl, extracted with diethyl ether, dried ($MgSO_4$), and concentrated (10.30 g, 94% yield) The product was sufficiently pure to be used without further purification and was spectroscopically identical to that previously reported [15].

1-(1-Methylcyclohexyl)cyclopenta-1,3-diene (IIb). A solution of 6,6-pentamethylenefulvene (10.0 g, 60.6 mmol) in diethyl ether (15 ml) was added to a solution of 1.5 M methyllithium (40.0 ml, 60.0 mmol) in diethyl ether at 0°C and the mixture was stirred for 2 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried ($MgSO_4$), and concentrated. Distillation at reduced pressure afforded pure product as an oil:

8.60 g (88%); b.p. 85-87°C (12 mmHg). IR (neat): 3065, 2900, 2730, 2660, 1600, 1520, 1450 cm^{-1}. ^{1}H NMR (60 MHz, CDC1$_3$): δ 6.60-5.80 (m, 3H); 2.80 (m, 2H); 1.70-1.10 (m, 10H); 0.92 (s, 3H). UV-Vis (hexanes): λ_{max} 246.3 nm (3.23).

Tetracyanoethylene adduct. 1-(1-Methylcyclohexylkyclopenta-1,3-diene (0.67 g, 4.90 mmol) and TCNE (0.80 g, 4.90 mmol) were stirred in acetone (2 ml) for 2 h. The solvent was removed and the resulting solid recrystallized (benzene/ petroleum ether) to provide pure product as a colorless solid: 0.58 g (39%); m.p. 83-85°C. ^{1}H NMR (60 MHz, CDC1$_3$): δ 6.70-5.90 (m, 1H); 4.20-3.80 (m, 2H); 2.25 (m, 2H); 2.10-1.20 (m, 13H). Anal. Found: C, 74.21; H, 6.15; N, 19.26. $C_{18}H_{18}N_4$ calcd.: C, 74.46; H, 6.25; N, 19.30%.

2-Cyclohexy1-6,6-dimethylfulvene (IIIa). 1-Cyclohexylcyclopenta-1,3-diene (5.00 g, 34.0 mmol), acetone (1.80 g, 31.0 mmol) and pyrrolidine (3.30 g, 46.0 mmol) were stirred in methanol (31 ml) for 3 h. Glacial acetic acid (2.9 ml) was added followed by water (50 ml) and the mixture was extracted with diethyl ether, dried ($MgSO_4$) and concentrated. Chromatography on silica using hexanes as eluent afforded pure product as an orange oil; 3.50 g (73%). IR (neat): 3100, 3060, 2900, 1640, 1450 cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6): δ 6.46 (dd, 1 H, J = 5.33, 2.00 Hz); 6.37 (dd, 1H, J = 5.33, 1.35 Hz); 6.12 (dd, 1H, J = 5.33, 1.35 Hz); 2.29 (m, 1H); 2.10 (s, 6H); 1.88 (brd, 2H); 1.75 (m, 2H); 1.40-1.13 (m, 6H). ^{13}C NMR (50.3 MHz, CDC1$_3$): δ 152.5, 146.6, 142.2, 131.5, 121.1, 112.9, 38.9, 32.7, 26.5, 26.4, 22.8, 22.7.

Tetracyanoethylene adduct (IVa). 2-Cyclohexy1-6,6-dimethylfulvene (0.50 g, 2.70 mmol) and TCNE (0.36 g, 2.80 mmol) were stirred in acetone (2 ml) for 4 h, concentrated and the resulting solid recrystallized (acetone/ petroleum ether) to provide pure product as a colorless solid: 0.63 g (73%); m.p. 148-150°C. ^{1}H NMR (200 MHz, CDCI$_3$): δ 6.18 (m, 1H); 4.35 (dd, 1H, J = 3.3, 1.9 Hz); 4.30 (m, 1H); 2.36-1.97 (m, 11H); 1.76 (s, 6H). Found: C, 75.82; H, 6.52; N, 17.67. $C_{18}H_{18}N_4$ calcd.: C, 75.92; H, 6.37; N, 17.70%.

2-(1-Methylcyclohexyl)-6, 6-dimethylfulvene (IIIb). 1-(1-Methylcyclohexyl)cyclopenta-1,3-diene (5.00 g, 31.0 mmol), acetone (1.80 g, 31.0 mmol) and pyrrolidine (3.30 g, 46.0 mmol) were stirred in methanol (31 ml) for 3 h. Glacial acetic acid (2.9 ml) was added followed by water (50 ml) and the mixture was extracted with diethyl ether, dried ($MgSO_4$) and concentrated. Chromatography on silica using hexanes as eluent afforded pure product as an orange oil: 3.50 g (73%). IR (thin film): 3100, 3075, 2900, 2662, 1645, 1575, 1450 cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6): δ 6.49 (dd, 1H, J = 5.46, 2.19 Hz); 6.46 (dd, 1H, J = 5.46, 1.81 Hz); 6.18 (dd, 1H, J = 2.19, 1.81 Hz); 2.12 (s, 3H); 2.11 (s, 3H); 1.82 (m, 2H); 1.53-1.35 (m, 8H); 1.09 (s, 3H); 155.7, 146.3, 142.2, 130.5, 121.2, 113.1, 37.4, 35.6, 27.8, 26.4, 22.8, 22.7. UV-Vis (hexanes): λ_{max} 271.8 (4.31), 266.1 (4.31) nm.

Tetracyanoethylene adduct (IVb). 2-(1-Methyl-cyclohexyl-6,6-dimethylfulvene (0.60 g, 3.0 mmol) and TCNE (0.38 g, 3.0 mmol) were stirred in acetone (2 ml) for 3 h, concentrated and the resulting solid recrystallized (benzene/ petroleum ether) to provide pure product as a colorless solid: 0.58 g, (59%); m.p. 122-124°C. ^{1}H NMR (60 MHz, CDCI$_3$): δ 1.75 (s, 6H); 1.70-1.30 (m, 10H); 0.70 (s, 3H). Anal. Found: C, 75.97; H, 6.63; N, 16.76. $C_{20}H_{22}N_4$ calcd.: C, 76.33; H, 6.71; N, 16.96%.

2-t-Butyl-6,6-dimethylfulvene (IIIc). 1-t-Butylcyclopenta-1,3-diene (7.40 g, 60.0 mmol), acetone (3.50 g, 60.0 mmol) and pyrrolidine (6.40 g, 90 mmol) were stirred in methanol (60 ml) for 1 h. Glacial acetic acid (5.5 ml) was added followed by water (100 ml) and the mixture was extracted with diethyl ether, dried ($MgSO_4$) and concentrated. Distillation at reduced pressure afforded pure product as an orange oil: 8.40 g (93%); b.p. 76-80°C (5 mmHg). IR (neat): 2980, 1645, 1445 cm^{-1}. ^{1}H NMR (500 MHz, acetone-d_6): δ 6.25 (dd, 1H, J = 2.21, 1.57 Hz); 6.58 (dd, 1H, J = 5.43, 1.57 Hz); 6.60 (dd, 1H, J = 5.43, 2.21 Hz); 2.12 (s, 3H); 2.11 (s, 3H); 1.14 (s, 9H). ^{13}C NMR (50.3 MHz, CDCl$_3$): δ 156.5, 146.8, 141.9, 130.5, 121.3, 111.7, 32.1, 29.7, 22.7, 22.6; UV-Vis (hexanes): λ_{max} 351.2 (2.50), 271.4 (4.28), 264.8 (4.28) nm. MS: *m/z* (relative intensity) 162 (9), 147 (33), 132 (10), 119 (13), 107 (10), 105 (11), 91 (13), 86 (45), 77 (11), 71 (18)k, 69 (30), 66 (100). This compound has been previously reported [17].

2-Cyclohexy1-6,6-pentamethylenefulvene (IIId). 1-Cyclohexylcyclopenta-1,3-diene (10.30 g, 69.2 mmol), cyclohexanone (6.80 g, 69.3 mmol) and pyrrolidine (7.30 g, 100 mmol) were stirred in methanol (70 ml) for 15 h. Glacial acetic acid (6.2 ml) was added followed by water (100 ml) and the mixture was extracted with diethyl ether, dried ($MgSO_4$) and concentrated. Chromatography on silica using hexanes as eluent afforded pure product as an orange oil: 7.80 g (50%); m.p. 34-37°C. IR (neat): 2930, 2860, 1680, 1450 cm^{-1}. ^{1}H NMR (500 MHz, benzene-d$_6$): δ 6.50 (dd, 1H, *J* = 5.41, 2.21 Hz); 6.40 (dd, 1H, *J* = 5.41, 1.52 Hz); 6.16 (dd, 1H, *J* = 1.85, 2.21 Hz); 2.59 (m, 4H); 2.27 (m, 1H); 1.85 (m, 2H); 1.77 (m, 2H); 1.65 (m, 6H); 1.40-1.09 (m, 6H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 154.7, 152.5, 139.1, 131.6, 120.5, 112.4, 39.0, 33.5, 33.4, 32.7, 28.5, 28.5, 26.6, 26.5, 26.4. UV-Vis (hexanes): λ_{max} 351.2 (Sh), 276.8 (4.34), 268.8 (4.34) nm.

Tetracyanoethylene adduct (IVd). 2-Cyclohexy1-6,6- pentamethylenefulvene. (0.38 g, 3.0 mmol) and TCNE (0.65 g, 3.0 mmol) were stirred in acetone (2 ml) for 2 h, concentrated and recrystallized (benzene/ diethyl ether) to provide pure product as a colorless solid: 0.62 g, (60%); m.p. 126-128°C. ^{1}H NMR (200 MHz, $CDC1_3$): δ 6.17 (m, 1H); 4.36 (dd, 1H, *J* = 3.2, 1.2 Hz), 4.33 (m, 1H); 2.35-0.89 (m, 21H). Anal. Found: C, 75.95; H, 6.72; N, 15.63. $C_{23}H_{24}N_4$ calcd.: C, 77.50; H, 6.78; N, 15.72%.

2-(1-Methylcyclohexy0-6,6-pentamethylenefulvene (IIIe). 1-(1-Methylcyclohexyl)cyclopenta-1,3-diene (8.00 g, 49.0 mmol), cyclohexanone (4.80 g, 49 mmol) and pyrrolidine (5.20 g, 76 mmol) were stirred in methanol (45 ml) for 24 h. Glacial acetic acid (4.4 ml) was added followed by water (100 nil) and the mixture was extracted with diethyl ether, dried ($MgSO_4$) and concentrated. Chromatography on silica using hexanes as eluent afforded pure product as an orange oil: 6.70 g (56%); m.p. 38-40°C. IR (neat): 3080, 2940, 2860, 1680, 1450 cm^{-1}. ^{1}H NMR (500 MHz, acetone-*d*$_6$): δ 6.50 (dd, 1H, *J* = 5.41, 2.17 Hz); 6.49 (dd, 1H, *J* = 5.41, 1.52 Hz); 6.22 (dd, 1H, *J* = 1.85, 2.17 Hz); 2.60 (m, 4H); 2.82 (m, 2H); 1.76-1.36 (m, 14H); 1.09 (s, 3H). ^{13}C NMR (50.3 MHz, $CDC1_3$): δ 155.7, 154.3, 139.3, 130.6, 120.6, 112.5, 37.4, 35.7, 33.4, 33.3, 28.5, 28.4, 27.6, 26.6, 26.5, 22.6. UV-Vis (hexanes): λ_{max} 352.6 (Sh), 276.1 (4.46), 267.4 (4.46) nm.

Tetracyanoethylene adduct (IVe). 2-(1-Methylcyclohexyl)-6,6-pentamethylenefulvene (0.60 g, 2.5 mmol) and TCNE (0.32 g, 2.5 mmol) were stirred in acetone (2 ml) for 4 h, concentrated and recrystallized (diethyl ether/ hexane) to provide pure product as a colorless solid: 0.52 g, (57%); m.p. 99-101°C. ^{1}H NMR (60 MHz, $CDC1_3$): δ 6.30 (m, 1H); 4.40 (m, 2H); 2.40-1.30 (m, 20H); 1.20 (s, 3H). Anal. $C_{24}H_{26}N_4$ calcd.: C, 77.80; H, 7.07; N, 15.128%. Found: C, 77.22; H, 7.00; N, 14.77.

2-t-Butyl-6,6-pentamethylenefulvene (IIIf). 1-t-Butylcyclopenta-1,3-diene (5.00 g, 41.0 mmol), cyclohexanone (4.00 g, 41.0 mmol) and pyrrolidine (4.30 g, 61.0 mmol) were stirred in methanol (40 ml) for 24 h. Glacial acetic acid (3.7 ml) was added followed by water (75 ml) and the mixture was extracted with diethyl ether, dried ($MgSO_4$) and concentrated. Chromatography on silica using hexanes as eluent afforded pure product as a orange oil: 6.20 g (75%); m.p. 2426°C. IR (neat); 3100, 3060, 2900, 1640, 1450 cm^{-1}. ^{1}H NMR (500 MHz, acetone-*d*$_6$): δ 6.54 (m, 1H); 6.49 (m, 1H); 6.17 (m, 1H); 2.56 (m, 4H); 1.65 (m, 6H); 1.16 (s, 9H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 156.7, 154.6, 139.3, 130.7, 120.8, 111.4, 33.5, 33.4, 32.3, 29.9, 28.6, 28.5, 26.7. UV-Vis (hexanes): λ_{max} 350 sh (2.64), 275.7 (4.39), 267.7 (4.38) nm. MS: *m/z* (relative intensity) 202 (32), 187 (89), 145 (26), 131 (20), 128 (20), 119 (100), 105 (21), 91 (42), 77 (23).

Tetracyanoethylene adduct (IVf). 2-t-Butyl-6,6-pentamethylenefulvene (0.50 g, 2.5 mmol) and TCNE (0.32 g, 2.5 mmol) were stirred in acetone (2 ml) for 3 h, concentrated and recrystallized (benzene/ petroleum ether) to provide pure product as a colorless solid: 0.45 g, (55%); m.p. 128-130°C. ^{1}H NMR (60 MHz, $CDC1_3$): δ 6.40 (m, 1H); 4.50 (m, 2H): 2.50-2.00 (m, 4H); 2.00-1.50 (m, 6H); 1.20 (s, 3H). Anal. Found: C, 76.03; H, 6.73; N, 16.66. $C_{21}H_{22}N$ calcd.: C, 76.32; H, 6.72; N, 16.96%.

E- and Z-2-t-butyl-6-t-butylfulvene (IIIg). 1-t-Butylcyclopenta-1,3-diene (3.60 g, 30 mmol), trimethylacetaldehyde (2.50 g, 29.0 mmol) and pyrrolidine (6.30 g, 89.0 mmol) were refluxed in methanol (30 ml) for 16 h. Glacial acetic acid (4.4 ml) was added followed by water (50 ml) and the mixture was extracted with diethyl ether, dried ($MgSO_4$) and concentrated. Distillation at reduced pressure afforded pure product as an orange oil:

1.90 g (34%); b.p. 120-140°C (0.05 mmHg). The product was spectroscopically identical to that previously reported [16].

2-t-Butyl-4-cyclohexylcyclopenta-1,3-diene (Va): method a. 2-t-Butyl-6,6-pentamethylenefulvene (3.10 g, 15.0 mmol) in diethyl ether (25 ml) was added dropwise to a solution of lithium aluminum hydride (0.73 g, 19.0 mmol) in diethyl ether (50 ml) and the mixture was stirred for 0.75 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried ($MgSO_4$), and concentrated. The cyclopentadiene was sufficiently pure to be used for further syntheses: 2.10 g, (70%). ^{1}H NMR (60 MHz, $CDC1_3$): δ 6.20-5.60 (m, 2H); 2.75 (brs, 2H); 2.20-1.05 (m, 11H); 1.05 (s, 9H). IR (neat): 3060, 2900, 2740, 2665, 1620, 1559 cm^{-1}. UV-Vis (hexanes): λ_{max} 255.2 nm (3.71).

2-t-Butyl-4-cyclohexylcyclopenta-1,3-diene (Va): method b. 2-Cyclohexyl-6,6-dimethylfulvene (21.80 g, 116.0 mmol) in diethyl ether (50 ml) was added drop-wise to a solution of 1.6 M methyl lithium (96.0 ml, 152.0 mmol) in diethyl ether at 0°C and the mixture was stirred for 2 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried ($MgSO_4$), and concentrated. Distillation at reduced pressure afforded pure product as an oil: 20.40 g (86%); b.p. 95-105°C (0.05 mmHg). The product was spectroscopically identical to that prepared by method a.

Tetracyanoethylene adduct. 2-t-Butyl-4-cyclohexylcyclopenta-1,3-diene (0.50 g, 2.45 mmol) and TCNE (0.31 g, 2.45 mmol) were stirred in acetone (2 ml) for 4 h, concentrated and recrystallized (benzene/ petroleum ether) to provide pure product as a colorless solid: 0.31 g (38%); m.p. 143-145°C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.15 (m, 1H); 3.90 (m, 2H); 2.50-1.20 (m, 13H); 1.20 (s, 9H). Anal. Found: C, 75.42; H, 7.15. $C_{21}H_{24}N_4$ calcd.: C, 75.87; H, 7.28%.

2-i-Propyl-4-cyclohexylcyclopenta-1,3-diene (Vb). 2-Cyclohexyl-6,6-dimethylfulvene (2.40 g, 13.0 mmol) in diethyl ether (25 ml) was added dropwise to a solution of lithium aluminum hydride (0.57 g, 15.0 mmol) in diethyl ether (30 ml) and the mixture was stirred for 4 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried ($MgSO_4$), and concentrated. Distillation at reduced pressure afforded pure product: 1.90 g (80%), b.p. 110-115°C (0.05 mmHg). ^{1}HNMR (60 MHz, $CDCl_3$): δ 6.30-5.80 (m, 2H); 2.87 (brs, 2H); 2.50 (m, 1H); 2.00-1.20 (m, 11H); 1.10 (d, 6H). IR (neat): 3060, 2960, 2930, 2860, 2740, 2680, 1625, 1560, 1450 cm^{-1}. UV-Vis (hexanes) λ_{max} 254.3 nm (3.67).

2-i-Propyl-4-t-butylcyclopenta-1,3-diene (Vc). 2-t-Butyl-6,6-dimethylfulvene (6.10 g, 40.0 mmol) in diethyl ether (25 ml) was added dropwise to a solution of lithium aluminum hydride (1.80 g, 47.0 mol) in diethyl ether (50 ml) and the mixture was stirred for 1 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried ($MgSO_4$), and concentrated. Distillation at reduced pressure afforded pure product: 4.50 g, (68%); b.p. 88-95°C (5 mmHg). ^{1}H NMR (200 MHz, $CDCl_3$): δ 623-5.76 (m, 2H); 2.90 (m, 2H); 2.66 (m, 1H); 1.15 (m, 15H). IR (neat): 3060, 2960, 2860, 2740, 2680, 1620, 1460 cm^{-1}. UV-Vis (hexane): λ_{max} 253.4 nm (3.66). MS: *m/z* (relative intensity) 164 (47), 149 (98), 147 (16), 121 (54), 119 (18), 107 (100) 93 (60), 91 (98).

Bis-2,4-cyclohexylcyclopenta-1,3-diene (Vd). 2-Cyclo-hexyl-6,6-pentamethylenefulvene (6.20 g, 27.0 mmol) in THF (25 ml) was added dropwise to a solution of lithium aluminum hydride (1.20 g, 32.0 mol) in THF (50 ml) and the mixture was stirred for 18 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried ($MgSO_4$), and concentrated. Distillation at reduced pressure afforded pure product as an oil: 4.70 g (76%); b.p. 130°C (2 mmHg). ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.40-5.60 (m, 2.4H); 2.50 (brs, 1.6H); 2.00-0.50 (m, 22H). IR (neat): 3060, 2900, 2660, 1610, 1555, 1445 cm^{-1}. UV-Vis (hexanes): λ_{max} 253.4 nm (3.73). MS: *m/z* (relative intensity) 230 (50), 162 (35), 147 (100) 119 (31), 117 (50), 115 (31), 105 (63).

2,4-Bis-(1-methylcyclohexya-cyclopenta-1,3-diene (Ve). 2-(1-Methylcyclohexyl)-6,6-pentamethylenefulvene (4.00 g, 16.50 mmol) in THF 915 ml) was added dropwise to a solution of 1.5 M methyllithium (14.0 ml, 21.0 mmol) in THF (20 ml) at 0°C and the mixture was stirred for 2 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried ($MgSO_4$), and concentrated. Distillation at reduced pressure afforded pure product as an oil: 2.90 g (67%); b.p. 120-125°C (0.05 mmHg). IR (neat): 3060, 2920, 2850, 2740, 2660, 1610, 1550, 1450 cm $^{-1}$. ^{1}H NMR (60 MHz, CDCl$_3$): δ 5.90-5.40 (m, 2H); 2.52 (br s, 2H); 1.50-0.90 (m, 20H); 0.75 (s, 6H). UV-Vis (hexanes): λ_{max} 254.3 nm (3.76).

2-t-Butyl-4-cyclohexylcyclopenta-1,3-diene (Vf). 2-t-Butyl-6,6-pentamethylenefulvene (3.10 g, 15.0 mmol) in diethyl ether (25 ml) was added dropwise to a solution of lithium aluminum hydride (0.73 g, 19.0 mmol) in diethyl ether (50 ml) and the mixture was stirred for 0.75 h. The reaction mixture was quenched with water extracted with diethyl ether, dried (MgSO$_4$), and concentrated. The cyclopentadiene was sufficiently pure to be used in further synthesis: 2.10 g (70%). ^{1}H NMR (60 MHz, CDCl$_3$): δ 6.20-5.60 (m, 2H); 2.75 (brs, 2H); 2.20-1.05 (m, 11H); 1.05 (s, 9H). IR (neat): 3060, 2900, 2740, 2665, 1620, 1559 cm^{-1}. UV-Vis (hexanes): λ_{max} 255.2 nm (3.71).

1-t-Butyl-3-neopentylcyclopentadiene (Vg). 2-t-Buty1- 6-t-butylfulvene (1.90 g, 10.0 mmol) in diethyl ether (25 ml) was added dropwise to a solution of lithium aluminum hydride (0.50 g, 13.0 mol) in diethyl ether (25 ml) and the mixture was stirred for 1 h. The reaction mixture was quenched with water, extracted with diethyl ether, dried (MgSO$_4$), and concentrated: 1.30 g (68%); b.p. 120-140°C (0.05 mmHg). ^{1}H NMR (60 MHz, CDCI$_3$): δ 6.31-5.72 (m, 2H); 2.91 (brs, 2H); 2.22 (brs, 2H); 1.12 (s, 9H); 0.90 (s, 9H). IR (neat) 3040, 2900, 2720, 1510, 1450 cm $^{-1}$. UV-Vis (hexanes): λ_{max} 256.1 nm (2.64).

1-t-Butylcyclopenta-1,3-diene (IIc) and bis-2,4-t-butylcyclopenta-1,3-diene (Vh). A solution of 6,6-dimethylfulvene (45.6 g, 0.43 mol) in diethyl ether (75 ml) was added to a solution of 1.5 M methyllithium in diethyl ether (358 ml, 0.538 mol) and the mixture was stirred for 1 h. t-Butyl bromide (53.0 ml, 0.46 mol) in THF (400 ml) was added over a 0.5 h, period, and the mixture was refluxed for 60 h. The reaction was poured onto ice and ammonium chloride, extracted with diethyl ether, dried (MgSO$_4$) and concentrated. Distillation at reduced pressure afforded t-butylcyclopentadiene as a colorless oil: 7.35 g (14%), b.p. 53-56°C (20 mmHg) and bis-2,4-t-butylcyclopentadiene: 29.50 g (52%): b.p. 72-75°C (15 mmHg). The products were spectroscopically identical to that previously reported [19].

1-Cyclohexylcyclopenta-1,3-diene (IIa) and bis-2,4- cyclohexylcyclopenta-1,3-diene (Vd). A solution of 6,6-pentamethylenefulvene (9.00 g, 61.5 mmol) in THF (10 ml) was added to a solution of lithium aluminum hydride (3.10 g, 62.0 mmol) in THF (100 ml) and the mixture was stirred for 2 h. Cyclohexyl bromide (13.30 g, 81.9 mmol) was added, and the mixture was refluxed for 8 h. The reaction was poured onto 1 M HC1, extracted with diethyl ether, dried (MgSO$_4$) and concentrated. Distillation at reduced pressure afforded cyclohexylcyclopentadiene as a colorless oil: 0.9 g (10%), b.p. 50-52°C (12 mmHg) and bis-1,3-cyclohexylcyclopentadiene: 4.90 g (35%): b.p. 110-115°C (12 mmHg).

Bis(η^5-1-t-Buty1-3-cyclohexylcyclopentadienyldicarbonyliron) (VIa). 1-t-Butyl-3-cyclohexylcyclopentadiene (18.6 g, 91.0 mmol), iron pentacarbonyl (62.7 g, 320 mmol) and norbomene (33.0 g, 350 mmol) were re-fluxed in isooctane (80 ml) for 40 h. The solution was filtered through celite, concentrated and the residue was purified by chromatography on silica with dichloromethane/ hexane (1: 3) to afford pure product as a red solid: 19.9 g (69%); m.p. 132-137°C. ^{1}H NMR (200 MHz, CDC1$_3$): δ ^{1}H NMR 4.98 (m, 2H); 4.21 (m, 2H); 3.46 (m, 1H); 3.36 (m, 1H); 2.66-2.51 (m, ^{2}H); 2.16-2.08 (m, 2H); 1.80-1.10 (m, 18H); 1.36 (s, 18H). IR (hexane): 1991, 1947, 1775 cm^{-1}. Anal. Found: C, 64.36; H, 7.44. C$_{34}$H$_{46}$0$_4$Fe$_2$ calcd.: C, 64.78; H, 7.35%.

Bis(η^5-1-isopropy1-3-cyclohexylcyclopentadienyldicarbonyliron) (VIb). 1-Isopropyl-3-cyclohexylcyclopentadiene (0.95 g, 5.0 mmol), iron pentacarbonyl (3.50 g, 17.5 mmol) and norbomene (1.80 g, 19.1 mmol) were refluxed in isooctane (80 ml) for 40 h. The solution was filtered through celite, concentrated and the residue was purified by chromatography on silica with dichloromethane/ hexane (1: 3) to afford pure product as a red solid: 0.75 g (50%); m.p. 140-145°C. ^{1}H NMR (200 Mhz, CDCl$_3$): δ 4.90 (br s, 2H); 3.83 (m, 2H); 3.77 (m, 2H); 2.94 (septet, 2H, J = 6.9 Hz); 2.63-2.47 (m, 2H); 2.15-1.00 (m, 20H); 1.26 (d, 6H, J = 6.9 Hz); 1.17 (d, 6H, J = 6.9 Hz). IR (hexane): 1990, 1945, 1775 cm^{-1}. Anal. Found: C, 63.12; H, 7 11 C$_{34}$H$_{42}$O$_4$Fe$_2$ calcd.: C, 63.81; H, 7.03%.

Bis(η^5-1-t-butyl-3-isopropylcyclopentadienyldicarbonyliron) (VIc). 1-t-Butyl-3-isopropylcyclopentadiene (1.50 g, 9.10 mmol), iron pentacarbonyl 96.30 g, 32.0 mmol) and norbomene (3.30 g, 35 mmol) were refluxed in isooctane (16 ml) for 40 h. The solution was filtered through celite, concentrated and the residue was purified by chromatography on silica with dichloromethane/hexane (1 : 3) to afford pure product as a red solid: 0.32 g (13%); m.p. 112-116°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.00 (m, 1H); 4.82 (m, 1H); 4.26 (m, 1H); 4.20 (m, 1H); 3.45 (m, 1H); 3.35 (m, 1H); 2.94 (br septet, 2H, J = 6.8 Hz); 1.37 (br s, 18H); 1.29 (d, 6H, J = 6.8 Hz); 1.17 (d, 6H, J = 6.8 Hz). IR (hexane): 1999, 1950, 1780 cm^{-1}. MS: *m/z* (relative intensity) 550 (1) 494 (35), 434 (36), 420 (63), 406 (38), 219 (100), 147 (22), 91 (25), 56 (30). HRMS for the monomer $C_{14}H_{19}FeO_2$ calcd.: 275.0734. Found; 275.0741. The parent ion of the dimer was not observed in the EI HRMS although a low resonance spectrum indicated a low intensity peak at 550 amu.

Bis(η^5-1-t-buty1-3-neopentylcyclopentadienyldicarbonyliron) (VIg). 1-t-Butyl-3-neopentylcyclopentadiene (0.96 g, 5.0 mmol), iron pentacarbonyl (3.50 g, 17.5 mmol) and norbomene (1.80 g, 19.1 mmol) were re-fluxed in isooctane (8.8 ml) for 40 h. The solution was filtered through Celite, concentrated and the residue was purified by chromatography on silica with dichloromethane/ hexane (1: 3) to afford pure product as a red solid: 0.30 g (20%); m.p. 130-132°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.74 (m, 2H); 4.46 (m, 2H); 3.40 (m, 2H); 2.16 (br s, 4H); 1.32 (s, 9H); 0.83 (s, 9H). IR (hexane): 1999, 1950, 1785 cm^{-1}. Anal. Found: C, 62.95; H, 7.81. $C_{32}H_{46}O_4Fe_2$ calcd.: C, 63.38; H, 7.65%.

Bis(η^5-bis-t-butylcyclopentadienyldicarbonyliron) (VIh). Bis-t-butylcyclopentadiene (5.38 g, 30 mmol) and diironnonacarbonyl (8.53 g, 30 mmol) were refluxed in hexane for 12 h. The solution was concentrated and the residue was crystallized from dichloromethane to afford pure product as red needles: 2.45 g (14%), m.p. 144-148°C. The product was spectroscopically identical to that previously reported [22].

Bis(η^5-bis-trimethylsilylcyclopentadienyldicarbonyliron) (VIi). Bis-trimethylsilylcyclopentadiene (5.38 g, 30 mmol) and diironnonacarbonyl (8.53 g, 30 mmol) were refluxed in hexane for 12 h. The solution was concentrated and the residue was crystallized from pentane to afford pure product as red needles: 0.40 g (20%), m.p. 174-176°C. The product was spectroscopically identical to that previously reported [23].

1,1',3,3'-Tetrakiscyclohexylferrocene (XII). A solution of 2.6 M butyllithium (5.20 ml, 13.5 mmol) in diethyl ether was added dropwise to bis-1,3-cyclohexylcyclopentadiene (3.10 g, 13.5 mmol) in diethyl ether (100 ml) at 0°C. After 0.5 h, anhydrous $FeCl_2$ (prepared from $FeCl_3$ (0.732 g, 4.51 mmol) and Fe (1.26 g, 22.5 mmol) in refluxing THF) was added and the mixture was stirred at room temperature for 8 days. Saturated ammonium chloride was added and the mixture was extracted with diethyl ether, dried ($MgSO_4$) and concentrated. Chromatography on silica using hexanes as eluant followed by recrystallization from hexanes provided pure product as an orange solid: m.p. 145-148°C; 0.50 g (11%). ^{1}H NMR (500 MHz, toluene-d_8): δ 3.97 (s, 6H); 2.34-1.14 (m, 44H). IR (CCl_4): 2920, 2840, 1540 cm^{-1}. UV-Vis (hexanes): λ_{max} 436.9 nm (2.14), 212.1 (4.57). MS: *m/z* (relative intensity) 514 (100) 430 (5), 348 (6), 134 (2), 55 (15). Anal. Found: C, 79.50; H, 9.95. $C_{34}H_{50}Fe$ calcd.: C, 79.36, H, 9.79%.

Bis-[1,3-(1-methylcyclohexyl)cyclopentadienyl]tricarbonylmethylmolybdenum (XIII). A solution of 2.5 M butyllithium (3.7 ml, 9.3 mmol) in hexane was added to a solution of bis-1,3-0-methylcyclohexylkyclopentadiene (2.37 g, 9.1 mmol) in THF (20 ml) at 0°C. After 1 h, a solution of tris(propionitrile)tricarbonylmolybdenum (3.14 g, 9.1 mmol) in THF (50 ml) was added *via* canula and the resulting mixture was refluxed for 4 h. A solution of iodomethane (1.29 g, 9.1 mmol) in THF (10 ml) was added and the mixture was stirred for 24 h. The resulting mixture was concentrated *in vacuo* and purified by chromatography on silica using petroleum ether as eluent to provide pure product as a yellow solid; m.p. 96-98°C (0.87 g, 21%). ^{1}H NMR (90 MHz, $CDC1_3$): δ 4.93 (s, 3H); 1.60-1.35 (m, 20H); 1.06 (s, 6H); 0.34 (s, 3H). Anal. Found: C, 61.27; H, 7.13. $C_{23}H_{32}O_3M$ calcd.: C, 61.01; H, 7.13%.

Bis-0,3-0-methylcyclohexy0cyclopentadienyil tricarbonylmethyl tungsten (XIV). A solution of 2.6 M butyl lithium (1.6 ml, 4.10 mmol) in diethyl ether was added to a solution of dry tetramethylethylenediamine

(TMEDA) (0.48 g, 4.10 mmol) and the complex was transferred via canula to a solution of bis-1,3-(1-methylcyclohexypcyclopentadiene (1.10 g, 4.10 mmol) in diethyl ether (15 ml) at 0°C. After 1 h., a solution of tris(propionitrile)tricarbonyl tungsten (1.76 g, 4.1 mmol) in THF (75 ml) was added *via* canula and the resulting mixture was refluxed for 3 h. A solution of iodomethane (0.57 g, 4.1 mmol) in THF (10 ml) was added and the mixture was stirred for 24 h. The resulting mixture was concentrated *in vacuo* and purified by chromatography on silica using dichloromethane/ petroleum ether (1: 9) as eluant to provide pure product as a yellow solid. m.p. 114-117°C (0.68 g, 31% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.03 (s, 3H); 1.69-1.39 (m, 20H); 1.16 (s, 6H); 0.44 (s, 3H). ^{1}H NMR (200 MHz, toluene-d_8): δ 4.91 (t, 1H, $J = 2.0$ Hz); 4.72 (d, 2H, $J = 2.0$ Hz); 1.71-1.32 (m, 20H); 1.11 (s, 6H); 0.74 (s, 3H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 217.8, 127.4, 88.7, 84.4, 39.9, 39.5, 34.5, 25.9, 24.5, 22.5, 22.4, - 32.6. IR (hexanes): 2010, 1925 cm^{-1}. UV-Vis (hexanes): λ_{max} 308.5 nm (3.40). MS: *m/z* (rel intensity) 540 (14), 512 (14), 464 (85) 434 (100), 216 (25), 194 (30), 178 (29), 97 (50), 55 (82). Anal. Found: C, 50.92; H, 6.21. $C_{23}H_{32}O_3W$ calcd.: C, 51.21; H, 5.96%.

Notes:

** The cyclopentadienes are always synthesized as mixtures of double bond isomers.
* cyc = cyclohexyl: Mecyc-1-methylcyclohexyl.

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