kcal/mol).[12] A more reliable value of K_3 was obtained by competition. Analysis of a 1:1:1 mixture of **1a**, **3**, and **4** (10 mM) in $CDCl_3$ gave $K_3/K_4 = ([\mathbf{1a}\text{-}3]/[\mathbf{1a}\text{-}4])([\mathbf{4}]_{free}/[\mathbf{3}]_{free}) = 105$,[13] and hence $K_3 = 1.2 \times 10^5\ M^{-1}$ ($\Delta G°_3 = -6.9$ kcal/mol). Similarly was shown the high preference of **3** over malonic acid (**2**) by a competitive binding in $CDCl_3$-CD_3OD (99:1).

In summary, a rigid and multidentate host **1** brings about an unprecedentedly large chain-length selectivity,[5c] $K_3/K_4 = 105$ ($\Delta\Delta G° = 2.8$ kcal/mol). The two-point hydrogen bonding is at least primarily responsible for the stability of the glutaric acid complex, although steric factors may also come into play.[14] The fact that $\Delta G°_3 < 2\Delta G°_5$ or $2\Delta G°_6$ indicates that an ideal two-point interaction is far more favorable than two independent one-point interactions.

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Supplementary Material Available: Evaluation of binding constants K (1 page). Ordering information is given on any current masthead page.

(12) Supplementary Material shows details of the evaluation of K's.

(13) The distribution of **1a**-**3**, **1a**-**4**, $\mathbf{3}_{free}$, and $\mathbf{4}_{free}$ was found to be independent of the order of addition of **1a**, **3**, and **4**, indicating reversibility of the complex formation process (eq 1).

(14) CPK models indicate that **3** in its most extended conformation ideally fits for the two-point interaction (refer to **7**); the significant ring current effects on the ^1H and ^{13}C resonances of bound **3** suggest a possible contribution of σ-π interactions to $\Delta G°_3$. If **4** is to be fixed via a similar two-point interaction, it must undergo bending of its pentamethylene backbone with freezing of rotations around two additional C-C bonds as compared with the case of **3**. This may result in an induction of steric strain, a loss of attractive σ-π interactions, and/or a significant loss in entropy as possible sources of $\Delta\Delta G°$ = 2.8 kcal/mol.

Di-*tert*-butylcyclopentadiene and Tri-*tert*-butylcyclopentadiene

Clifford G. Venier* and Edward W. Casserly*

Technology Division, Pennzoil Products Company
P.O. Box 7569, The Woodlands, Texas 77387

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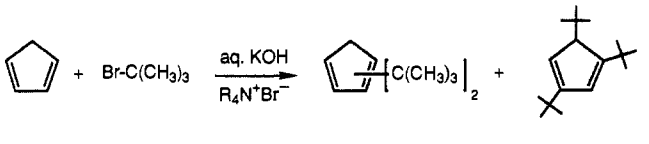
Bis(1,1-dimethylethyl)cyclopentadiene (**1**) and tris(1,1-dimethylethyl)cyclopentadiene (**2**) can be prepared in high yields by phase-transfer-catalyzed alkylation. This is the first reported preparation of tri-*tert*-butylcyclopentadiene. It is also the first example of carbon alkylation under phase-transfer conditions using a tertiary halide.



1a; 1,3-
1b; 1,4-
1c; 2,5-

2

In connection with a more general study of the preparation of multiply alkylated cyclopentadienes,[1] we have discovered that cyclopentadienes can be readily alkylated by tertiary halides under phase-transfer-catalysis conditions using quaternary ammonium halides. In view of the extensive interest in new cyclopentadiene ligands, we are reporting the easy preparation of these two molecules in preliminary form.

Steric effects on the reactivity of organometallic complexes as a function of *phosphine* ligand structure have received much attention, and useful catalysts have resulted.[2] Much less work on the steric effects of changing cyclopentadiene ligand structure has been reported,[3] primarily because sterically bulky cyclopentadienes have not been readily available.

Tumanov et al.[11] report that equilibria for ion-radical formation between tungsten-cyclopentadienyl complexes and TCNE or TCNQ are very sensitive to the bulk of substituents on the cyclopentadienyl ring. Changing from *n*-butylcyclopentadienyl as ligand to *tert*-butylcyclopentadienyl changes the equilibrium constants by a factors of up to 100. The changes correlate to the Charton steric parameter, υ.

A good measure of the steric effect of a substituent is the ligand cone angle, Θ. Tolman[2] calculated a Θ for unsubstituted cyclopentadienyl of 136°. Inspection of models for di- and tri-*tert*-butylcyclopentadienyls suggests that their cone angles may be 180° or more.

Phase-transfer-reaction conditions are reported to give only alkenes from tertiary alkyl halides.[12-14] The surprising fact that reactions of stoichiometric ratios of cyclopentadienyl[15-17] and *tert*-butylcyclopentadienyl anions[18,19] with *tert*-butyl bromide give about 50% yields of the *tert*-butylated products suggested to us that phase-transfer *tert*-butylation of cyclopentadiene with an excess of the *tert*-butyl bromide might give high yields of di-*tert*-butylcyclopentadienes. This proved to be the case.

Although the literature preparations of di-*tert*-butylcyclopentadiene use *tert*-butyl bromide and cyclopentadiene as the ultimate starting materials, they do so in two steps with preformed cyclopentadienyl anions.[18,19] Such procedures are cumbersome and involve the inconvenience of reaction in a dry, airless environment.

Tri-*tert*-butylcyclopentadiene has not been reported previously, but tetra-*tert*-butylcyclopentadiene has been prepared in connection with the synthesis of tetra-*tert*-butyltetrahedrane.[20] The preparation is a very long one.

The phase-transfer procedure we have found useful is as follows. KOH (aqueous 50%), *tert*-butyl bromide, and freshly distilled cyclopentadiene in the mole ratio 40:5:1 plus Adogen 464 (1 g per mole of KOH) were stirred together and heated to 60 °C for 75 min and 100 °C for an additional 45 min. (*CAUTION*: sudden foaming sometimes occurs.) The cooled reaction mixture was diluted with pentane, washed with water, and dried over $MgSO_4$. Pentane is removed in vacuo. The crude residue contains the product, Adogen 464, and amine byproducts of Adogen 464 de-

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Table I. ^{13}C Nuclear Magnetic Resonance Assignments[a]

position	1a[b]	1b[b]	2
C-1	159.1	155.8	159.6
C-2	123.7	123.2	129.2
C-3	156.1	123.2	153.5
C-4	119.4	155.8	126.2
C-5	39.1	38.2	62.9
$C(CH_3)_3$;	33.1 (1)	33.1 (1)	34.0 (5)
ring position	32.1 (3)		33.8 (1)
in parentheses			31.8 (3)
$C(CH_3)_3$;	29.7 (1)	30.9 (1)	32.0 (1)
ring position	30.9 (3)		30.3 (3)
in parentheses			29.6 (5)

[a] Assignments made by ^{13}C SAT (Varian), ^1H-^{13}C NOE difference, and DEPT techniques. [b] Analysis performed on a mixture of **1a** and **1b**. The relative intensities of peaks in each region of the spectrum were used to assign resonances to either **1a** or **1b**.

composition. Chromatography of the crude material over silica gel yielded di-*tert*-butylcyclopentadiene; overall calculated yield, 90% based on starting cyclopentadiene.

Although tri-*tert*-butylcyclopentadiene can be prepared directly by the reaction of cyclopentadiene and *tert*-butyl bromide, we have found it more convenient to prepare it by *tert*-butylation of di-*tert*-butylcyclopentadiene. The procedure is essentially the same as described above, but 55% aqueous KOH is used. The reaction is monitored by GC, and additional *tert*-butyl bromide and Adogen 464 are added as needed until about half of the mixture has been converted to **2**. After workup to remove KOH, Adogen 464, and amines, the di- and tri-*tert*-butylcyclopentadienes can be separated by distillation, yielding 50% recovered **1**, bp 100–105 °C at 30 Torr, and 30% **2**, bp 135–140 °C at 30 Torr.

Structure proofs relied primarily on ^{13}C NMR, although elemental analyses are consistent with the empirical formulas, $C_{13}H_{22}$ for di-*tert*-butylcyclopentadiene and $C_{17}H_{30}$ for tri-*tert*-butylcyclopentadiene. Chemical shifts and assignments are recorded in Table I. The ^{13}C NMR spectrum of **1a** has previously been reported.[19]

Di-*tert*-butylcyclopentadiene exists as a mixture, the two major isomers being **1a** and **1b** in a 3:1 ratio as determined by gas chromatography. The identity of the two isomers was easily assigned from the ^{13}C NMR spectra of mixtures by the relative intensities of the resonances and the symmetry of **1b**.[21]

Tri-*tert*-butylcyclopentadiene exists as a single isomer, 1,3,5-tris(1,1-dimethylethyl)cyclopentadiene. The downfield position of the ring C-5, 62.9 ppm, compared with that found in **1a** and **1b**, 39.2 ppm and 38.3 ppm, respectively, clearly signals that one of the *tert*-butyl groups is on C-5. The reported position of the C-5 carbon in tetra-*tert*-butylcyclopentadiene, 64.1 ppm,[20] in which one *tert*-butyl is also presumed to be on C-5, supports the assignment.

The predominance of the 1,3,5-isomer arises since it is the only arrangement that does not put *tert*-butyl groups on three adjacent carbons nor two *tert*-butyl groups on adjacent sp^2 carbons. For less sterically bulky substituents, *n*-alkyl groups, trialkyl derivatives are also predominantly single isomers, but they are the 1,2,4- rather than 1,3,5-isomers,[1] placing all three alkyl groups on sp^2 carbons.

The conditions under which these reactions are run, strong base in the presence of a phase-transfer catalyst, inevitably favor elimination reactions with tertiary substrates.[12-14] Consequently, the operation of previously recognized substitution mechanisms involving tertiary halides seems unlikely. The fact that alkylation competes so favorably with elimination argues for a unique reaction pathway involving cyclopentadiene prior to the rate-determining step. Although the delineation of the mechanism of this unique transformation would be interesting, we have no plans to do so at this time.

(21) A small amount of a third isomer, probably 2,5-di-*tert*-butylcyclopentadiene (**1c**) is also apparently present. Our colleague Dr. J. S. McKennis observed that, on standing, a sample of **1** yielded a crystalline precipitate, **3**, mp 120–123 °C. Gas chromatography showed a single peak, neither **1a** nor **1b**, but at only a slightly longer retention time, suggesting an isomeric $C_{13}H_{22}$ compound. Dr. McKennis believes that all of this data is consistent with **3** being the self-Diels–Alder dimer of **1c**. The ^{13}C NMR spectrum of **3** showed at least 17 unique carbons of the 18 expected for the dimer. Note that **1c** has both a diene and an ene with no *tert*-butyl substituents on the reactive carbons. Work to confirm the structure of **3** is in progress.

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Synthesis of Substituted Pyridinones from the Combination of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with Phosphinimines and Alkynes

Chad A. Mirkin, Kuang-Lieh Lu, Thomas E. Snead, and Gregory L. Geoffroy*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Arnold L. Rheingold

Department of Chemistry, The University of Delaware
Newark, Delaware 19716

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The pyridinone ring is an integral unit of many important molecules. 2-Pyridinones in particular have therapeutic value[1a,2] and are versatile synthetic intermediates for many alkaloids.[2] A continuing need exists for improved synthetic routes to pyridinones that tolerate a wide variety of substituents with a high degree of regiospecificity in ring substitution. Previous organometallic routes to 2-pyridinones have generally involved regiospecific coupling of two alkynes with an isocyanate, yielding tri- or pentasubstituted products.[3] Reported herein is a complementary but mechanistically different metal-assisted route to mono-, di-, and trisubstituted 2-pyridinones involving reaction of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with phosphinimines and alkynes.

We earlier reported the high-yield reaction of $Fe_2(\mu\text{-}CH_2)(CO)_8$ with phosphinimines to form the binuclear complexes **1** shown in Scheme I.[4] These complexes have since been found to readily insert alkynes into the Fe–carbon bond under photochemical conditions[5] to give the ferrapyridine complexes **2a–g**. These latter species were isolated in 72–87% yields as microcrystalline solids and have been spectroscopically characterized,[6] with complex **2e** (R^1, R^2, R^3 = Ph) fully defined by an X-ray diffraction study, Figure 1.[7] Terminal alkynes insert regiospecifically into the

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(6) **2e**: Anal. C, H. IR (CH_2Cl_2): ν_{CO} = 2061 (m), 2013 (vs), 1988 (s), 1956 (w) cm^{-1}. MS: m/z = 575 (M^+). ^1H NMR (CD_2Cl_2): δ 8.13 (d, 1 H, J = 5.1 Hz, C*H*), 7.59–6.92 (m, 10 H, 3Ph), 3.64 (d, 1 H, J = 5.1 Hz, C*H*). ^{13}C NMR (C_6D_6): δ 211.0, 208.7, 208.0 (CO), 181.0 (dd, N=*C*H, $^1J_{CH}$ = 167.7 Hz, $^2J_{CH}$ = 2.6 Hz), 179.0 (m, *C*Ph), 154.9–121.8 (Ph), 109.0 (d, *C*Ph, $^2J_{CH}$ = 4.0 Hz), 54.1 (dd, *C*H, $^1J_{CH}$ = 158.9 Hz, $^2J_{CH}$ = 12.0 Hz).

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