Synthesis of $[C_5(CH_3)_4H]CH_2CH_2CH_2P(C_6H_5)_2$: A Novel Heterodifunctional Ligand Possessing Both a Tetramethylcyclopentadiene and a Remote Diphenylphosphine Functionality

Dennis M. Bensley, Jr., Eric A. Mintz,*[1] and Susan J. Sussangkarn

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

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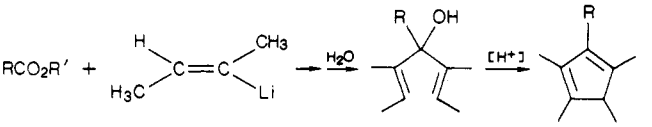
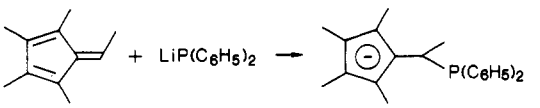
In recent years transition metal organometallic complexes incorporating the pentamethylcyclopentadienyl ligand have proven to be useful in the investigation of the reduction of both free and transition metal bound CO, and the activation of H_2 and C–H bonds.[2-10] Given the reactivity patterns that have been exhibited by transition metal complexes incorporating the pentamethylcyclopentadienyl ligand, it is surprising that functionalized tetramethylcyclopentadienyl ligands have not been widely prepared and utilized in organometallic chemistry.

Casey et al. have reported that treatment of lithium tetramethylcyclopentadienide with $P(p\text{-}C_6H_4CH_3)_2Cl$ produces $[C_5(CH_3)_4H]P(p\text{-}C_6H_4CH_3)_2$.[11] However, the use of the lithium tetramethylcyclopentadienide for the preparation of substituted tetramethylcyclopentadienes has been greatly restricted due to high basicity and relatively poor nucleophilicity.[12] The majority of the substituted tetramethylcyclopentadienes $[C_5(CH_3)_4H]R$ (R = $(CH_2)_nCH_3$, n = 1–3),[12,13] $CH_2C_6H_5$,[12,14] C_6H_5,[13] $CH(CH_2CH_3)C_6H_5$,[15] $CH_2CH_2[C_5(CH_3)_4H]$,[16] $p\text{-}C_6H_4[C_5(CH_3)_4H]$,[17] $p\text{-}C_6H_4C_6H_4[C_5(CH_3)_4H]$,[17] have been prepared by the dicondensation of the appropriately substituted ester with 2-butenyllithium. However, this method has not led to

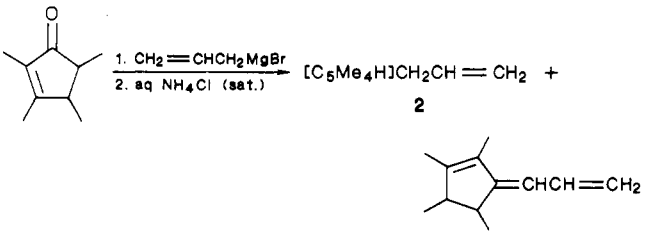


the preparation of heteroatom-substituted ligands. We have recently shown that the addition of $LiPPh_2$ to 1,2,3,4,6-pentamethylfulvene is a convenient route for the preparation of $[C_5(CH_3)_4H]CH(CH_3)P(C_6H_5)_2$.[18] We report here a convenient high yield synthesis of 3-(tetramethylcyclopentadiene)diphenylphosphinopropane, a precursor for the preparation of remote phosphine substituted tetramethylcyclopentadienyl transition metal complexes.

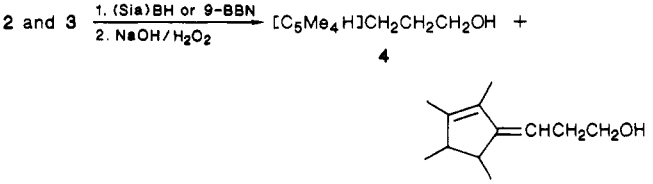


Results and Discussion

Treatment of 2,3,4,5-tetramethylcyclopent-2-enone (**1**) with allylmagnesium bromide in ether, followed by workup with saturated aqueous ammonium chloride, produces 3-(tetramethylcyclopentadienyl)-1-propenes (three tautomers) (**2**) and 3-(2,3,4,5-tetramethylcyclopent-2-en-1-ylidene)-1-propene (**3**) in 95% yield based on **1**. Tautomers, **2** and **3**, need not be separated, since the exocyclic double bond in **3** has been found to isomerize into the ring system later in the synthesis (vide infra).



The reaction of the mixture of **2** and **3** with an excess of disiamylborane or 9-borabicyclo[3.3.1]nonane (9-BBN) followed by the usual workup with NaOH and H_2O_2 produces 3-(tetramethylcyclopentadienyl)-1-propanols (**4**) (three tautomers) and 3-(2,3,4,5-tetramethylcyclopent-2-en-1-ylidene)-1-propanol (**5**) in 93–99% yield.



Treatment of **4** and **5** with *p*-toluenesulfonyl chloride in pyridine, followed by the usual workup, produces 3-(tetramethylcyclopentadienyl)-1-(*p*-tolylsulfonyl)propane (**6**) (three tautomers) in 74% yield, with no detectable amount of the exocyclic double bond tautomer as determined by ^1H and ^{13}C NMR. Apparently, during the acidic workup, the exocyclic double bond isomerizes into the ring producing only **6**.

(1) Present address: Department of Chemistry, School of Arts and Sciences, Atlanta University, Atlanta, GA 30314-4381.

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$$\text{4 and 5} \xrightarrow[\text{pyridine}]{p\text{-TsCl}} \underset{6}{[C_5Me_4H]CH_2CH_2CH_2OTs}$$

Reaction of **6** with lithium diphenylphosphide in THF produces the three tautomers of 3-(tetramethylcyclopentadienyl)-1-(diphenylphosphino)propanes (**7**) in 72% yield based on **6** (53% based on **1**) as an air-sensitive yellow oil. Phosphine **7** can be converted to the corresponding phosphine oxides by treatment with air in benzene, and treatment of the phosphine oxides with $LiAlH_4$ in ether at 0 °C will convert the phosphine oxides back to phosphine **7**.

$$\text{6} \xrightarrow[\text{THF}]{(C_6H_5)_2PLi} \underset{7}{[C_5Me_4H]CH_2CH_2CH_2P(C_6H_5)_2}$$

Spectral Characterization

The ^1H NMR spectra of compounds **2–7** were complicated by the presence of three to four tautomers. The ^{13}C NMR spectrum of the mixture of **2** and **3** clearly show the presence of four tautomers: For compounds **2** (three tautomers), there are three methine, three methylene, three olefinic methine, and three olefinic methylene resonances present in the spectrum. For **3** there are two methine, two olefinic methine, and one olefinic methylene resonance present in the spectrum. An appropriate number of methyl and olefinic carbon resonances for **2** and **3** are also present in the spectrum (see the Experimental Section).

The ^{13}C NMR spectra of alcohols **4** and **5** show the presence of four tautomers. For compounds **4** (three tautomers), there are three methine resonances and nine methylene resonances present in the spectrum. For compound **5** there is one olefinic methine resonance and two methylene resonances present in the spectrum. An appropriate number of methyl and olefinic carbon resonances for **4** and **5** are also present in the spectrum (see the Experimental Section).

The ^{13}C NMR spectrum of tosylates **6** shows the presence of only three tautomers. There are three methine, nine methylene, one tosyl methyl, and the appropriate number of methyl, aromatic, and olefinic carbons resonances present in the spectrum.

The ^{13}C NMR spectrum of phosphines **7** shows the presence of three isomers. There are three aliphatic methine resonances, nine methylene resonances all coupled with phosphorus, and the appropriate number of methyl, olefinic, and aromatic carbons present in the spectrum. The $^{31}P\{^1H\}$ NMR spectrum also shows three resonances at −17.8, −17.9, and −18.0 ppm.

2,3,4,5-Tetramethylcyclopent-2-enone, **1**, has proven to be a convenient starting material for the high-yield preparation of remote phosphine **7**. We believe that the synthetic methodology presented in this paper will prove to be a general route for the preparation of remotely substituted tetramethylcyclopentadienes with a chain length of three or more carbons. However, this methodology is unsuitable for the high-yield preparation of the two carbon chain analogue, as treatment of **1** with vinylmagnesium bromide leads to the formation of a 5:1 mixture of 1,2,3,4,6-pentamethylfulvene and vinyltetramethylcyclopentadienes.[18] Further work is in progress to explore the utility of **7** in the preparation of new mononuclear and binuclear transition metal organometallic complexes.

Experimental Section

All operations were performed under vacuum or an atmosphere of dry nitrogen or argon on a double-manifold, high-vacuum line or in a Vacuum Atmospheres glovebox under a nitrogen atmosphere. Solvents were prepurified by distillation from Na/K alloy under nitrogen. Allylmagnesium bromide (Aldrich), pyridine (Fisher), *p*-toluenesulfonyl chloride (Aldrich), chlorodiphenylphosphine (Aldrich), and *n*-butyllithium (Aldrich) were used as purchased.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 270, 67.8, and 109.25 MHz, respectively, on a JEOL GX 270 NMR spectrometer. Spectra were measured at ambient temperature in C_6D_6 or $CDCl_3$, with residual solvent peaks or tetramethylsilane as an internal standard. The ^{31}P NMR spectra are reported relative to external 85% H_3PO_4. Elemental analysis were performed by Microlytics, S. Deerfield, MA.

Treatment of 2,3,4,5-Tetramethylcyclopent-2-enone (1) with Allylmagnesium Bromide. To 210 mL (400 mmol) of 1.9 M allylmagnesium bromide, in a 1000-mL three-necked round-bottom flask equipped with a nitrogen inlet adapter, condenser, and a septum-capped, pressure-equalizing addition funnel was added dropwise via an addition funnel 50.9 g (368 mmol) of 2,3,4,5-tetramethylcyclopent-2-enone[19] (**1**) in 175 mL of dry ether at room temperature. The resulting solution was allowed to stir overnight. The reaction mixture was then quenched with approximately 50 mL of saturated aqueous ammonium chloride. The organic layer was washed once with saturated aqueous ammonium chloride, separated, and dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under vacuum to give 57.0 g (351 mmol) of **2** and **3** (95% yield based on **1** as a light yellow oil). Compounds **2** and **3** were found to be thermally labile and were stored at 0 °C until used. This mixture was suitable for use without further purification. IR (neat): 3080 (w), 2960 (vs), 2920 (vs), 2800 (vs), 1635 (m), 1620 (m), 1445 (s), 1375 (m), 990 (m), 960 (w), 910 (m), 885 (m). ^1H NMR (270 MHz, C_6D_6): δ 0.95 (d, CH_3, 8.1 Hz), 0.96 (d, CH_3, 8.1 Hz), 1.05 (d, CH_3, 8.1 Hz), 1.18 (d, CH_3, 8.1 Hz), 1.60 (s, CH_3), 1.67 (s, CH_3), 1.75 (s, CH_3), 1.78 (s, CH_3), 1.80 (s, CH_3), 1.84 (s, CH_3), 2.05 (m, CH), 2.40 (t, CH), 2.48 (q, CH), 2.58 (q, CH), 2.92 (d, CH_2), 2.93 (d, CH_2), 3.08 (dd, CH_2), 4.95 (m, CH_2, olefinic), 5.12 (d, CH_2, olefinic), 5.72 (m, CH, olefinic), 5.90 (d, CH, olefinic), 6.70 (m, CH, olefinic). $^{13}C\{^1H\}$ NMR (67.5 MHz, C_6D_6): δ [10.2, 11.0, 11.2, 11.3, 11.7, 11.8, 11.9, 12.1, 13.3, 14.1, 14.5, 19.6, 22.1] (CH_3), [30.4, 31.4, 32.5] (CH_2), [42.9, 48.0] (CH in 3), [50.2, 52.0, 55.9] (CH in 2), [114.0, 114.3, 114.6, 115.3] (CH_2, olefinic), [117.1, 121.8, 125.3, 134.9, 137.0] (CH, olefinic), [131.5, 134.0, 134.2, 135.1, 135.6, 135.8, 136.2, 138.0, 138.5, 139.3, 139.4, 146.4, 155.7] (olefinic). Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.82; H, 11.38.

Preparation of 3-(Tetramethylcyclopentadienyl)-1-propanols, $[C_5(CH_3)_4H]C_3H_6OH$ (4 and 5). To a 2000-mL three-necked, round-bottom flask equipped with a nitrogen inlet adapter, condenser, and a septum-capped, pressure-equalizing addition funnel was added 57.0 g (351 mmol) of **2** and **3** in 125 mL of THF. To the addition funnel was added 386 mmol of a 9-borabicyclo[3.3.1]nonane (9-BBN) solution, prepared from 386 mmol of 1 M BH_3·THF and 47.4 mL of 1,5-cyclooctadiene in 193 mL of THF.[20] The 9-BBN solution was then added dropwise at room temperature. The reaction mixture was then stirred for 3 h at room temperature and then cooled to 0 °C in an ice–water bath. Approximately 24 mL of H_2O was added dropwise, followed by 125 mL of 3M NaOH added all at once. Then 126 mL of 30% hydrogen peroxide was slowly added dropwise to the solution. The reaction mixture was heated to 50 °C in a water bath for 1 h and then cooled to room temperature. The aqueous layer was saturated with 276 g of K_2CO_3. The organic layer was then separated from the aqueous layer, and the THF was removed under vacuum. The resulting yellow oil was dissolved in 400 mL of ether and then washed with 6 × 100 mL of H_2O to remove *cis*-1,5-cyclooctanediol. The organic layer was then washed once with aqueous saturated sodium chloride, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed under vacuum to give 62.7 g (348 mmol) of **4** and **5** (99% yield based on **2** and **3**) as a viscous yellow oil. This mixture was suitable for use without further purification. IR (neat): 3350 (br s), 2960 (vs), 2910 (vs), 2850 (vs), 1635 (w) 1435 (s), 1375 (s), 1165 (w), 1110 (w), 1050 (s), 910 (w), 860 (w), 830 (w). ^1H NMR (270 MHz,

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$CDCl_3$): δ 0.94 (d, CH_3, 6.8 Hz), 0.96 (d, CH_3 6.8 Hz), 0.99 (d, CH_3, 6.8 Hz), 1.58 (s, CH_3), 1.67 (s, CH_3), 1.73 (s, CH_3), 1.76 (s, CH_3), 1.77 (s, CH_3), 1.80 (s, CH_3), 2.00 (m, CH), 2.22 (t, CH_2), 2.35 (q, CH), 2.45 (t, CH), 3.05 (bs, OH), 3.44 (t, CH_2), 3.54 (t, CH_2), 3.59 (t, CH_2), 5.00 (t, CH olefinic). $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$): δ [9.9, 10.8, 10.9, 11.4, 11.5, 12.7, 13.9, 14.0, 19.0, 21.1] (CH_3), [21.9, 22.3, 22.5, 23.7] (CH_2 γ to OH in 4a and CH_2 β to OH in 4), [32.0, 32.3, 33.1] (CH_2 γ to OH in 4b and 4c, and CH_2 β to OH in 5), [62.2, 62.3, 62.6, 62.8] (CH_2 α to OH), [42.0, 49.2, 51.0, 51.3, 55.4] (CH), [110.7] (olefinic, CH in 5), [130.3, 133.2, 133.7, 134.6, 134.8, 135.5, 137.8, 137.9, 138.1, 138.4, 141.5, 143.5, 154.7] (olefinic). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.84; H, 11.19.

Preparation of 3-(Tetramethylcyclopentadienyl)-1-(*p*-tolylsulfonyl)propanes, $[C_5(CH_3)_4H]CH_2CH_2CH_2OSO_2[p\text{-}CH_3(C_6H_4)]$ (6). Dry pyridine (400 mL) was added to 53.7 g (298 mmol) of **4** and **5** in a 1000-mL round-bottom flask. The resulting solution was stirred and cooled to 0 °C in an ice–water bath. To this solution was added 71.2 g (373 mmol) of *p*-toluenesulfonyl chloride. The flask was stoppered and placed in a refrigerator (approximately 3 °C). After 2 days, the solution had turned black and large crystals of pyridine hydrochloride had formed. The solution was then poured into a 1000-mL beaker containing 300 g of ice. The solution was stirred, and a purple oil formed. The oil was taken up in 300 mL of ether, and the water layer was separated from the organic layer. The aqueous layer was washed with 4 × 150 mL of diethyl ether. The combined organic phase was then washed with 2 × 200 mL of cold, 1:1 HCl/water. The yellow organic phase was then washed with H_2O until neutral. The organic layer was then washed once with aqueous saturated sodium chloride, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed under vacuum to give 74.1 g (222 mmol) of **6** (74% yield based on **4** and **5**) as a brown viscous oil. Compound **6** is thermally unstable; however, it may be stored at 0 °C for several weeks. This mixture was suitable for use without further purification. IR (neat): 2940 (vs), 2900 (vs), 2840 (vs), 1635 (w), 1590 (w), 1435 (s), 1350 (s), 1165 (vs), 1090 (m), 1020 (w), 955 (m), 910 (m), 805 (m), 655 (m). ^1H NMR (270 MHz, $CDCl_3$): δ 0.91 (d, CH_3, 5.4 Hz), 0.95 (d, CH_3, 5.4 Hz), 1.40–1.60 (m, CH_2), 1.65 (s, CH_3), 1.70 (s, CH_3), 1.75 (s, CH_3), 1.80 (s, CH_3), 2.40 (m, CH), 2.00 (s, CH_3), 3.90 (t, CH_2), 4.00 (t, CH_2), 6.90 (d, Ar-*m*, 10.8 Hz), 7.80 (d, Ar-*o*, 10.8 Hz). $^{13}C\{^1H\}$ NMR (67.8 MHz, $CDCl_3$): δ [10.7, 10.8, 11.3, 11.4, 13.7, 13.9, 21.1] (CH_3), [21.3] (CH_3 tosyl), [21.3] (CH_2 γ to tosyl 6a), [21.6, 22.7, 23.0] (CH_2 β to tosyl), [28.4, 29.2] (CH_2 γ to tosyl in 6b and 6c), [69.8, 70.0, 71.0] (CH_2 α to tosyl), [48.9, 51.2, 54.8] (CH), [133.6, 144.4] (Ar-*i*), [127.5] (CH, Ar-*o*), [129.5] (CH, Ar-*m*), [132.7, 133.0, 134.2, 135.6, 135.8, 136.3, 138.2, 138.3, 139.3, 139.6] (olefinic).

Preparation of 3-(Tetramethylcyclopentadienyl)-1-(diphenylphosphino)propanes, $[C_5(CH_3)_4H]CH_2CH_2CH_2P(C_6H_5)_2$ (7). To 30 g (90 mmol of **6** in 150 mL of THF in a 500-mL, three-necked, round-bottom flask equipped with a nitrogen inlet adapter, condenser, and a septum-capped, pressure-equalizing addition funnel was added at 0 °C 90 mmol of a lithium diphenylphosphide solution via the addition funnel, prepared from 16.1 mL (90 mmol) of chlorodiphenylphosphine in 20 mL of THF and 2.61 g (376 mmol) of Li shavings in 100 mL of THF. The yellow-brown reaction mixture was then stirred overnight at room temperature. The THF was then removed under vacuum. The resulting yellow oil was taken up in 250 mL of diethyl ether and then washed with 2 × 100 mL of deoxygenated H_2O. The aqueous layer was separated from the organic layer, dried over anhydrous calcium chloride, and filtered, and the solvent was removed under vacuum. The resulting yellow oil was dissolved in dry hexane and filtered through Celite, and the solvent was removed under vacuum. Diphenylphosphine formed during the reaction sequence was removed by vacuum distillation at 80 °C (1×10^{-3} Torr) to give 22.6 g (65 mmol) of **7** (72% yield) as a viscous yellow oil. IR (neat): 3040 (s), 2940 (vs), 2900 (vs), 2840 (vs), 1940 (w), 1875 (w), 1800 (w), 1640 (m), 1580 (m), 1470 (s), 1425 (vs), 1370 (s), 1325 (w), 1300 (w), 1250 (m), 1175 (m), 1090 (s), 1060 (m), 1020 (s), 995 (m), 960 (m), 800 (m), 735 (vs), 695 (vs). ^1H NMR (270 MHz, C_6D_6): δ 1.00 (d, CH_3, 8.0 Hz), 1.05 (d, CH_3, 8.0 Hz), 1.23 (m, CH_2), 1.40–1.50 (m, CH_2), 1.74 (s, CH_3), 1.78 (s, CH_3), 1.82 (s, CH_3), 1.85 (s, CH_3), 1.87 (s, CH_3), 2.00 (t, CH_2), 2.06 (t, CH_2), 2.09 (t, CH_2), 2.42 (t, CH), 2.50 (m, CH), 7.13 (s, aromatic), 7.50 (m, aromatic). $^{13}C\{^1H\}$ NMR (67.8 MHz, C_6D_6): δ [11.2, 11.4, 11.7, 11.8, 11.9, 14.3, 14.4] (CH_3), [20.7] (CH_2 β to phosphine 7a, $J_{^{31}P-^{13}C}$ = 17.0 Hz), [26.3, 27.2] (CH_2 β to phosphine 7b and 7c, $J_{^{31}P-^{13}C}$ = 17.0 Hz), [27.4, 27.9, 28.0, 28.8, 29.2, 29.4] (CH_2 α and γ to phosphine, $J_{^{31}P-^{13}C}$ = 13.6 Hz), [49.5, 51.8, 56.4] (CH), [128.6] (Ar-*m*, $J_{^{31}P-^{13}C}$ = 6.8 Hz), [128.7] (Ar-*p*), [132.5, 133.0, 133.1] (Ar-*o*, $J_{^{31}P-^{13}C}$ 17.1 Hz), [138.3, 139.8, 140.0] (Ar-ipso, $J_{^{31}P-^{13}C}$ = 14.6 Hz), [133.8, 134.2, 135.0, 135.3, 135.8, 138.0, 138.1, 141.8] (olefinic). $^{31}P\{^1H\}$ NMR (109.25 MHz, C_6D_6): δ −17.8, −17.9, −18.0. Anal. Calcd for $C_{24}H_{29}P$: C, 82.72; H, 8.39. Found: C, 82.84; H, 8.39.

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Communications

Studies on the Enantioselectivity in $Bu_4N[Fe(CO)_3NO]$-Catalyzed Nucleophilic Substitution of Optically Active Allylic Carbonates with Malonate

Summary: The stereochemical outcomes of optically active allylic carbonates **2**, **5**, and **9** with malonate in the presence of iron catalyst **1** were determined. It was found that in every case the nucleophile predominantly attacked at the carbon atom where the leaving group was attached, and the corresponding prevailing regioisomer **3**, **6**, or **10** was obtained with high retention of configuration at the chiral center.

Sir: Among the various carbon–carbon-bond-forming reactions promoted or catalyzed by transition metals, allylic alkylation has been one of the most aggressively sought after. Accordingly, in recent years, extensive studies have been devoted to the regio- and stereochemistry of these allylic alkylation reactions catalyzed by different metal complexes, such as palladium,[1] molybdenum,[2] tungsten,[3] nickel,[4] iron,[5] etc., and the wide applications of these re-

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