Journal of Organometallic Chemistry, 229 (1982) 109—112
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ALKALI METAL SALTS OF PENTAPHENYLCYCLOPENTADIENIDE

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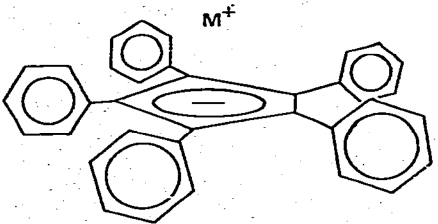
(Received June 23rd, 1981)

Summary

Synthetic procedures leading to isolable alkali metal salts of pentaphenylcyclopentadienide are described. The Cs, K, Na, and Li salts have been prepared and characterized by IR, UV, ^{13}C NMR, and by elemental analysis. The stability, structure, and potential utility of these alkali metal organometallic compounds are discussed.

Alkali metal salts of cyclopentadienide and substituted cyclopentadienides are of broad utility as ligands in organometallic chemistry. Recent work has emphasized the utility of substituted cyclopentadienyl ligands that possess steric hindrance or chelating properties [1,2]. In many cases, the metal complexes resulting from use of these ligands have enhanced stability as a result of the properties of these ligands. For example, pentamethylcyclopentadienyl complexes of transition metals and of both actinides and lanthanides have proven to have especially interesting chemistry [3,4]. Here we report a useful synthesis of isolable alkali metal salts of pentaphenylcyclopentadienide $(C_6H_5)_5C_5M$; M = Li, Na, K, and Cs) (1a—1d) and characterization of the resulting organometallic compounds by spectroscopy and elemental analysis. These hindered derivatives



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0022-328X/82/0000—0000/$02.75

of cyclopentadienyl should have interesting properties as ligands in organometallic chemistry. Previous examples of the use of pentaphenylcyclopentadienyl (PPCp) as a ligand include reports of the formation of (PPCp)Fe$(CO)_2$Br from Fe$(CO)_5$ and PPCpBr [5]; the formation of $(PPCp)_2$Mo from diphenylacetylene and Mo$(CO)_6$ under pressure [6]; the formation of $(\mu\text{-}C_6H_5C{\equiv}CC_6H_5)(PPCpPd)_2$ from diphenylacetylene and palladium acetate [7]; and the formation of $(PPCp)_2$Ni from nickel(0) and PPCp$^\cdot$ [8]. In several cases, enhanced stability was noted for the organometallic complexes of PPCp, perhaps because of the steric hindrance of the PPCp ligand.

Alkali metal salts of PPCp are readily prepared by one of two procedures (eq. 1 or 2). The lithium salt is accessible by reaction of n-butyllithium with

$$(C_6H_5)_5C_5H \quad + \quad C_4H_9Li \quad \xrightarrow{C_6H_5CH_3,\ 100^\circ C} \quad (C_6H_5)_5C_5Li \qquad (1)$$

$$(C_6H_5)_5C_5H \quad + \quad \text{Metal} \quad \xrightarrow[\text{Metal} = \text{Na, K, Cs}]{C_6H_5CH_3,\ 100^\circ C} \quad (C_6H_5)_5C_5\text{Metal} \qquad (2)$$

PPCpH in hot toluene. The other alkali metal salts of PPCp are conveniently formed by heating a suspension of PPCpH and the appropriate alkali metal in toluene. The product PPCpM was in each case isolated as a solid after cooling the toluene solution in which the reaction had been carried out.

The alkali metal salts of PPCp show greater stability in air than the corresponding salts of unsubstituted cyclopentadienide. Although we typically handled these compounds in an inert atmosphere, deliberate exposure of these alkali metal compounds to air did not lead to rapid decomposition; solid PPCpM gradually turned yellow only after several hours in air. Reaction of the PPCpM salts with THF solutions of HCl led, as expected, to PPCpH.

The enhanced stability of PPCpM salts is due in part to the electron-withdrawing character of the aryl substituents. However, spectroscopic data (Table 1) show that these aryl substituents do not stabilize the negatively charged carbons primarily through resonance. ^{13}C NMR spectra obtained for each alkali metal PPCpM in DMSO-d_6 were essentially identical and in every case, had resonances for the substituent aryl rings at chemical shifts in the δ 120—130 ppm region typical of aromatic carbons. ^{13}C NMR shifts of carbons bearing partial negative charge typically are more significantly affected by the negative charge [9]. We believe that the lack of significant shifts in these spectra reflect the

TABLE 1

^{13}C NMR SPECTRAL DATA FOR $(C_5H_6)_5C_5M$ [a]

Metal	^{13}C chemical shifts (ppm)				
Li	142.4 [b]	131.0	125.8	120.8	119.8 [b]
Na	142.3 [b]	131.2	126.2	121.1	119.8 [b]
K	142.3 [b]	131.2	126.2	121.1	119.8 [b]
Cs	142.3 [b]	131.0	125.9	120.9	119.8 [b]

[a] Obtained from 0.07 *M* solutions in DMSO-d_6. [b] ^1H-coupled spectra showed that this peak was due to a quaternary carbon.

inability of the substituent aryl rings to achieve the planar conformation necessary for efficient resonance stabilization of the negative charge in the cyclopentadienyl ring [10]. The ^{13}C NMR experiments demonstrated the high symmetry of I. Although PPCpH could have as many as 21 peaks in ^{13}C NMR (20 were resolved), I has only 5 peaks. The similarity of the ^{13}C NMR spectra of Ia—Id reflect the fact that the cations are not closely associated with the anions I under the conditions of our ^{13}C NMR experiments. Some slight differences were noted in the UV spectra of Ia—Id in THF.

These simple synthetic procedures make pure PPCp salts readily available as ligands for organometallic synthesis. Although the starting PPCpH is quite insoluble, the metal salts have reasonable solubility and should be useful as precursors of hindered organometallic complexes of transition metals and lanthanides [11].

Experimental

All reactions and operations were performed with the use of Schlenk techniques or a drybox with an atmosphere of dried, oxygen-free argon. Tetrahydrofuran (THF) was dried and freed of oxygen by distilling under argon from blue sodium benzophenone ketyl immediately prior to use. Toluene was degassed and distilled from sodium sand. Melting points were determined in sealed argon-filled capillaries. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Ultraviolet spectra were recorded on a Beckman Model 24 spectrophotometer. Solutions were kept in a special 1-cm quartz cuvette which had been fused to a Schlenk adapter so that the solutions could be maintained under an inert atmosphere. IR spectra were recorded on a Pye Unicam SP3-200 spectrophotometer as Nujol mulls between NaCl plates. The mulls were prepared in the drybox using dry, degassed Nujol. ^1H NMR spectra were obtained using either a Varian EM390 or FT-80A spectrometer. ^{13}C NMR spectra were obtained on a Varian FT-80A spectrometer. Chemical shifts in ^1H and ^{13}C NMR are reported as ppm relative to tetramethylsilane. Pentaphenylcyclopentadiene (PPCpH) was prepared following the method of Ziegler [14] and had m.p. 244—246°C. ^{13}C NMR spectra of PPCpH in DMSO-d_6 (0.05 M at 80°C) contained 13 peaks in the region δ124—132 ppm some of which were only partially resolved, 6 peaks in the region δ134—148 ppm, and a peak at δ61.3 ppm; ^1H NMR ($CDCl_3$) δ7.42—7.02(m), 5.06(s) ppm.

Preparation of pentaphenylcyclopentadienyl lithium (PPCpLi)

A suspension of 1 g (2.24 mmol) of PPCpH in 15 ml of toluene was prepared in a Schlenk tube and warmed to 100°C to produce a homogeneous clear solution. Then 1.65 ml of a 1.35 N solution of n-butyllithium in hexane was added dropwise over a 30-min period. Some precipitate formed and a gas was evolved. After continuing to stir the reaction mixture for an additional hour at 100°C, the solution was cooled and a precipitate of PPCpLi formed. The supernatant liquid was removed after centrifugation and the remaining solid PPCpLi was dried in vacuo at 70°C to give 0.9 g (90%) of an off-white powder; m.p. 340°C (dec); ^1H NMR (THF) δ 6.5—6.9(m) ppm; UV in THF (λ_{max} in nm, (ϵ)), 248 (9800), 265 (7000), 343 (3220); IR (cm^{-1}) 920, 790, 770, 730, and 700. Found: C, 91.98; H, 5.81; Li, 1.52. $C_{35}H_{25}Li$ calcd.: C, 92.92; H, 5.33; Li, 1.55%.

Preparation of pentaphenylcyclopentadienylsodium (PPCpNa), -potassium (PPCpK) and -cesium (PPCpCs)

A mixture of 13.4 g (30 mmol) of PPCpH, 0.64 g (28 mg-atom) of sodium and 200 ml of toluene was placed in a Schlenk tube and heated with vigorous stirring at 110°C. A solid gradually formed as gas was released as the metal disappeared. The reaction was continued until all of the metal disappeared at which time the reaction mixture was cooled to room temperature. The resulting suspension of PPCpNa was then centrifuged and the supernatant liquid removed. The solid PPCpNa was then dissolved in THF, recrystallized and dried in vacuo at 70°C to give 12.3 g (95%) of product. Similar procedures with potassium or cesium in place of sodium yielded 82% and 90% of PPCpK·THF and PPCpCs respectively.

The PPCpNa prepared according to the above procedure had m.p. 360°C (dec); ^{1}H NMR (THF) δ 6.5—6.9(m) ppm; UV in THF (λ_{max} in nm (ϵ)), 250 (17 700), 270 (11 800), 344 (3880); IR (cm^{-1}) 915, 795, 770, 735 and 700. Found: C, 88.17; H, 5.70; Na, 5.11. $C_{35}H_{25}Na$ calcd.: C, 89.75; H, 5.34; Na, 4.9%.

The PPCpK · THF prepared according to the above procedure had m.p. 250°C (dec); ^{1}H NMR (THF) δ 6.5—7.0(m) ppm; UV in THF (λ_{max} in nm, (ϵ)), 250 (28 000), 270 (18 300), 344 (6000); IR (cm^{-1}) 905, 800, 775, 735, 705, and 695. Found: C, 84.73; H, 6.10; K, 7.03. $C_{39}H_{33}K$ calcd.: C, 84.16; H, 5.93; K, 6.90%.

The PPCpCs prepared according to the above procedure had m.p. >400°C; ^{1}H NMR (THF) δ 6.5—6.9(m) ppm; UV in THF (λ_{max} in nm (ϵ)), 250 (64 000), 270 (46 700), 330 (11 300); IR (cm^{-1}) 900, 801, 775, 735, 705, 695. Found: C, 72.20; H, 4.58; Cs, 22.60. $C_{35}H_{25}Cs$ calcd.: C, 72.67; H, 4.33; Cs, 23.00%.

Acknowledgment

Acknowledgment is made to the Robert A. Welch Foundation for support of this research.

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