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A beneficial effect of ortho-substituents in the arylation of (benzene)tricarbonylmanganese(1 +) hexafluorophosphate(1 −)

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Abstract

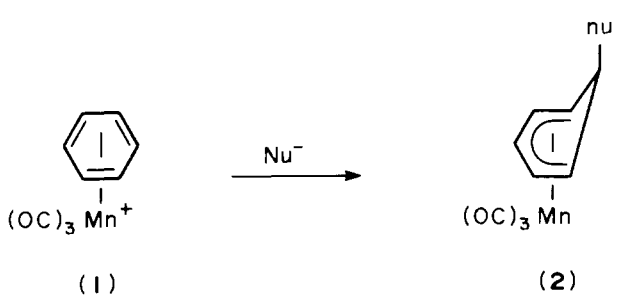
ortho-Substituted aryllithium and aryl Grignard reagents react with (benzene)manganesetricarbonyl cation (**1**) to give good yields of the expected ring adducts. The presence of the *ortho* substituent(s) appears to be necessary for the satisfactory outcome of the reaction with aryllithiums. This reactivity opens up the possibility of preparing novel heterocyclic structures via the initial reaction of **1** with functionalised metallated arenes.

Keywords: Manganese; Carbonyl; Arene complexes; Orthometallation; Metal carbonyl cations

1. Introduction

One reason why the reactivities of transition metal arene complexes continue to be an area of intense research activity is that high stereocontrol can be observed in reactions at the arene. It is therefore not surprising that methods have been devised to use this effect for more than a single manipulation. Thus, stepwise double additions to arene complexes of iron [1], or manganese [2] to give 5,6-*cis*-disubstituted cyclohexadienes have been carried out. A complementary mode of reaction to afford 5,6-*trans*-disubstituted cyclohexadiene derivatives from arene chromium complexes has also been developed [3].

The initial step in the manganese approach involves addition of nucleophiles to (arene)tricarbonylmanganese cations **1** to give the complexes **2**. Subsequent reaction of **2** with $NOPF_6$ results in replacement of CO by NO^+, thus regenerating a cationic complex which can react with a second nucleophile at the terminus of the dienyl system [2]. In order to exploit this approach most effectively for organic synthesis, a full understanding of the range and availability of suitable nucleophile types for reaction with (arene)tricarbonylmanganese cations is desirable. We now report that, in contrast to PhLi, aryllithium reagents containing substituents *ortho* to Li react with (benzene)tricarbonylmanganese(1 +) hexafluorophosphate (**1**) to give the desired ring adducts in good yield. This reaction opens a simple pathway to some novel heterocycle derivatives by placing a heteroatom containing functional group *ortho* to the site of metallation which is capable of acting as a second nucleophile. Indeed, such a nucleophile addition/reactivation/intramolecular nucleophile addition sequence has already been successfully employed in an approach to the synthesis of hippeastrine utilising (cyclohexadienyl)tricarbonyliron complexes and a functionalised metallated arene [4].



(1) (2)

2. Results and Discussion

Phenyllithium (30%) [5] and PhMgBr (80%) [6] were previously reported to react with **1** to give the *exo* ring adducts (**2a**, nu=Ph). In addition, low yields of ring adducts were reported in the reaction of PhLi or MeLi

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Table 1
Results of arylation of 1 with aryllithium reagents and aryl Grignard reagents

Entry	Nucleophile	Product	Conditions	Yield (%) [Ref.]
1	PhLi	**2a**	0°C, 10 min	30 [5]
2	PhMgBr	**2a**	0°C, 10 min	80 [6]
3	2-MeC_6H_4Li	**2b**	0°C–R.T.	81
4	2-MeC_6H_4MgBr	**2b**	0°C–R.T.	84
5	2-$OMeC_6H_4Li$	**2c**	0°C–R.T.	84
6	2-$OMeC_6H_4MgBr$	**2c**	0°C–R.T.	70
7	2,6-$(OMe)_2C_6H_3Li$	**2d**	35°C, 1h	85

with (arene)tricarbonylmanganese cations bearing functional substituents [7]. Thus Grignard reagents appear to have become the reagents of choice for the alkylation of **1** [6,8]. However, for appropriately substituted arenes, lithium reagents may be the most attractive choice owing to the possibility of forming the reagent via metallation techniques [9], avoiding the need for an aryl bromide precursor. We report here our findings that the presence of an *ortho* substituent on the metallated arene greatly increases the yield of the arylation of **1** by aryllithium reagents (Table 1).

First, some experiments were carried out to monitor the effect of introducing a methyl or methoxy group *ortho* to the site of metallation (Table 1, entries 3–6). As can be seen, both the Grignard and the lithium reagents gave good yields of the expected coupled products (**2b**; nu=2-MeC_6H_4, **2c**; nu=2-$OMeC_6H_4$). As previously reported [5], under the same conditions PhLi reacts less selectively to give **2a** (Nu=Ph) as the major product in only 30% yield.

Among other possible reaction pathways available to nucleophiles [10], attack at the carbonyl ligand of (arene)tricarbonylmanganese cations has previously been observed, and found to give acyl-type products which appear to become increasingly stable as the number of methyl groups present on the arene ring is increased [10,11]. Of particular relevance, PhLi has been reported to react with such cations (arene=mesitylene, C_6Me_6, C_6Me_5H) to afford mixtures of products derived from ring attack and CO attack [10,12]. It therefore seems that whereas PhLi reacts non-selectively with (arene)tricarbonylmanganese cations, the presence of an *ortho* substituent on the aryllithium increases the selectivity for ring attack.

Next, the reaction with **1** of 2,6-dimethoxyphenyllithium, prepared by the metallation route [9a] was carried out. Again, a good yield of the desired product (**2d**; nu=2,6-$(OMe)_2C_6H_3$) was obtained, but, the reaction required higher temperature and a longer reaction time, almost certainly as a result of the increased steric hindrance at the metallated arene. The product is a thermally stable compound melting sharply at 136°C. The same product would be more difficult to obtain by use of a Grignard reagent and such a route was not attempted. This reaction therefore demonstrates that for functionalised metallated arenes formation via orthometallation is the most suitable route. This work also emphasises that the balance between nucleophile attack on the arene ring and other reaction pathways is delicate, and in this case it is tilted towards *exo* ring attack simply by the introduction of an *ortho* substituent. This is a surprising effect, since one might have expected that the presence of an *ortho* substituent would lower the nucleophilicity of the lithium reagent and allow possible decomposition (i.e. by electron transfer [1]) to occur, thereby decreasing the proposition of ring attack [13]. However, in these examples the main effect of the increased bulk appears to be to inhibit detrimental side reactions. Thus, it seems likely that other sterically hindered lithium reagents may also work well for the alkylation of **1**.

3. Experimental Section

3.1. General

All experiments were carried out under an atmosphere of dry N_2. Ether and THF were dried and distilled prior to use. The ^1H NMR spectra were recorded on a Varian T-60A NMR spectrometer, and the IR spectra on a Perkin Elmer 577 IR spectrometer. Melting points were recorded with an electrothermal digital melting point apparatus. Elemental analyses were carried out at the Tübitak Research Centre, Gebze, Turkey. Bromobenzene, 2-bromoanisole, 2-bromotoluene and 1,3-dimethoxybenzene were purchased (Aldrich) and used as received. Grignard reagents and lithium reagents [9] were prepared as solutions in ether from the aryl bromide and Li or Mg by standard procedures unless otherwise specified. The concentrations of these reagents were determined by titration against 0.1 M HCl prior to use. Additions of the metallated arenes to **1** were carried out by the previously described procedures for phenyl addition (i.e. THF, 0°C for Grignard reagents; ether, 0°C for aryllithiums). The reactions were quenched by addition of 0.5 ml of dilute HCl, and crude products were isolated after extraction into ether.

3.2. Tricarbonyl[η^5-6-exo-(2-methylphenyl)cyclohexadienyl]manganese (2b)

Route A. After reaction of 2-methylphenyllithium (0.5 mmol) with **1** (72 mg, 0.2 mmol), work up, and solvent removal, a yellow residue (108 mg) was obtained. Crystallisation from pentane afforded the pure product (**2b**, 50 mg, 81%).

Route B. Reaction of 2-methylphenylmagnesium bromide (0.5 mmol) with **1** (72 mg, 0.2 mmol) followed

by work up and solvent removal afforded a yellow residue (110 mg). Crystallisation from pentane afforded the pure product (**2b**, 52 mg, 84%) m.p. 114–115°C. IR (KBr): 2005s, 1910s,br cm^{-1}. ^1H NMR ($CDCl_3$): δ: 2.33 (s, 3H, CH_3); 3.46 (t, 2H, J=6, H1 + H5); 4.02 (t, 1H, J=6, H6*endo*); 4.98 (t, 2H, J=6, H2 + H4); 5.75 (m, 1H, H3); 7.08 (m, 4H, Ar–H). Anal. Calc. for $C_{16}H_{13}MnO_3$: C, 62.35; H, 4.25. Found: C, 62.17; H, 4.25%.

3.3. *Tricarbonyl[η^5-6-exo-(2-methoxyphenyl)cyclohexadienyl]manganese (2c)*

Route A. Reaction of 2-methoxyphenyllithium (0.4 mmol, prepared from 2-bromoanisole and butyllithium) with **1** (54 mg, 0.15 mmol), followed by work up and crystallisation from ether/pentane, afforded the pure product (**2c**, 41 mg, 84%).

Route B. After reaction of 2-methoxyphenylmagnesium bromide (0.5 mmol) with **1** (72 mg, 0.2 mmol) a yellow residue (96 mg) was obtained and was subjected to column chromatography (1.2 cm (diam) × 5 cm, silica gel, petrol). One yellow band was eluted quickly. The solvent was removed form this band to afford **2c** as a yellow solid (45 mg, 70%). The product was recrystallised from pentane, mp. 119–120°C. IR (KBr): 2000s, 1895s,br, 1230m, 1025w cm^{-1}. ^1H NMR ($CDCl_3$): δ: 3.47 (t, 2H, J=6, H1 + H5); 3.78 (s, 3H, OCH_3); 4.20 (m, 1H, H6*endo*); 4.92 (t, 2H, J=6, H2 + H4); 5.68 (m, 1H, H3); 6.88 (m, 4H, Ar–H). Anal. Calc. for $C_{16}H_{13}MnO_4$; C, 59.27; H, 4.04. Found: C, 58.94; H, 3.85%.

3.4. *Tricarbonyl[η^5-6-exo-(2,6-dimethoxyphenyl)cyclohexadienyl]manganese (2d)*

After reaction of 2,6-dimethoxyphenyllithium [9a] (0.5 mmol) with **1** (54 mg, 0.15 mmol) and work up a residue (0.15 g) was obtained and was subjected to column chromatography [1 cm (diam) × 30 cm, silica gel, CH_2Cl_2/petrol (3%)]. One major yellow band was observed. This band was collected and afforded the pure product (**2d**, 45 mg, 85%) after solvent removal and crystallisation, m.p. 136°C. IR (KBr): 1995s, 1915s,br, 1240m, 1090m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.49 (t, 2H, J=6, H1 + H5); 3.73 (s, 6H, 2OMe); 4.50 (t, 1H, J=6, H6*endo*); 4.82 (t, 2H, J=6, H2 + H4); 5.62 (m, 1H, H3); 6.36 (d, 2H, J=8, Ar–H); 6.98 (t, 1H, J=8, Ar–H). Anal. Calc. for $C_{16}H_{13}MnO_4$: C, 57.64; H, 4.27. Found: C, 57.75; H, 4.18%.

Acknowledgements

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