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**Preliminary communication**

# PREPARATION AND REACTIVITY OF $\eta^6$-VERATROLEMANGANESE TRICARBONYL TETRAFLUOROBORATE

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## Summary

Reaction of pentacarbonylmanganese tetrafluoroborate with veratrole (1,2-dimethoxybenzene) affords $\eta^6$-veratrolemanganese tricarbonyl tetrafluoroborate in 66% yield. This complex does not react satisfactorily with alkyllithium compounds, but it does undergo highly regioselective reaction with the lithium enolate of cyclohexanone, *ortho* to the MeO substituent. The product was converted to 2-(2,3-dimethoxyphenyl)cyclohexanone, thereby giving a novel and unique method for regioselective functionalization of veratrole. Similarly, anisolemanganese tricarbonyl tetrafluoroborate, and 4-bromoveratrolemanganese tricarbonyl tetrafluoroborate were prepared and their reactivity toward the enolate nucleophile was examined.

Activation of aromatic compounds toward nucleophilic attack represents an attractive method for the synthesis of polysubstituted derivatives and, ultimately, might provide useful methodology for the synthesis of natural products. The use of arene chromium tricarbonyl complexes is now fairly well established [1], but these compounds undergo carbon—carbon bond formation only with very reactive nucleophiles, thereby limiting the degree to which deactivating substituents (OR, $NR_2$, etc.) may be attached to the ring. The corresponding arenemanganese tricarbonyl cations are much more reactive, leading to a potentially greater range of nucleophile additions, but have been little studied with regard to their synthetic capability [2]. Recent advances have been accomplished by Sweigart et al. [3] and these prompt us to disclose preliminary results of our own studies aimed at the functionalization of veratrole(1,2-dimethoxybenzene) (1) via its tricarbonylmanganese derivative **2a**.

The sensitivity of 1,2-dimethoxybenzene derivatives to aluminium chloride precludes [4] the use of the usual conditions ($BrMn(CO)_5$, $AlCl_3$, high temperature) for preparation of their $Mn(CO)_3$ derivatives, so we devised the following

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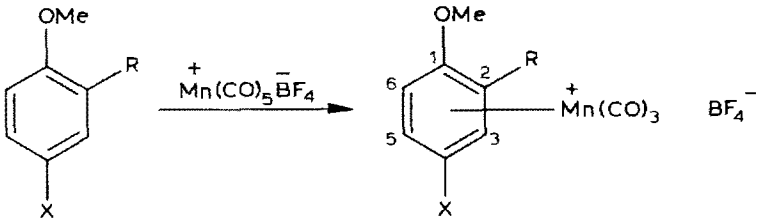



1

2a R = OMe, X = H

2b R = X = H

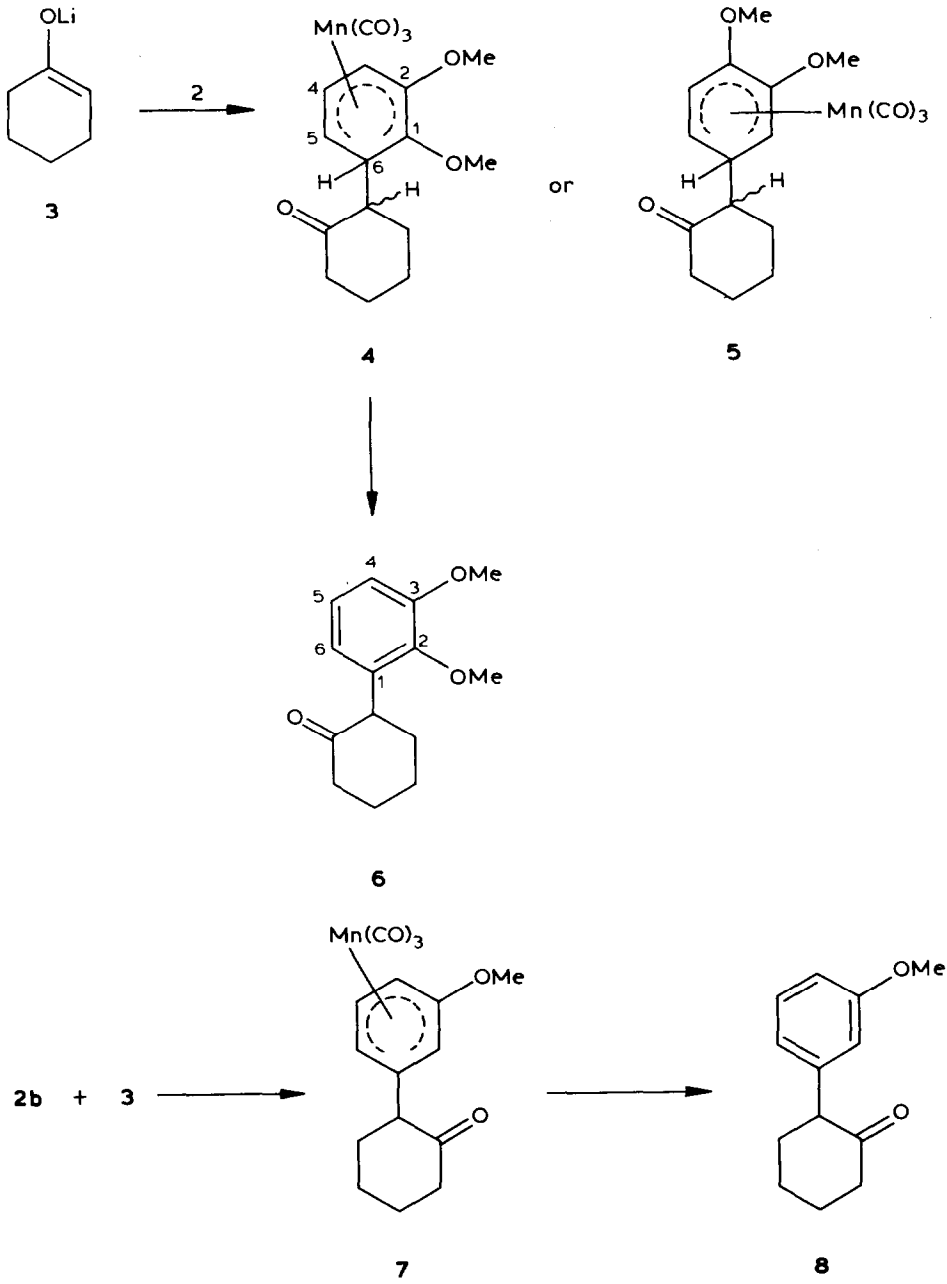
2c R = OMe, X = Br

alternative procedure, using pentacarbonylmanganese tetrafluoroborate [5], which should also be applicable to a wide range of polysubstituted aromatic compounds. A solution of bromomanganese pentacarbonyl (2.75 g) in dichloromethane (300 ml) was stirred vigorously under argon atmosphere and with exclusion of light, whilst silver tetrafluoroborate (2.0 g) was added. Stirring was continued under reflux for 3.5 h, the precipitate of AgBr removed by filtration, and the filtrate was concentrated to ca. 150 ml. Veratrole (3.2 g, 2.5 equiv.) was added and the mixture was stirred at reflux temperature under argon, with exclusion of light, for 3.5 h. The product **2a** (2.4 g, 66% based on $BrMn(CO)_5$) was isolated by evaporation of solvent, and precipitation with ether [6].

The reactivity of complex **2a** is somewhat different from that observed for the simpler arenemanganese tricarbonyl systems previously reported [2]. For example, reaction with PhLi or MeLi led only to extensive decomposition with no detectable formation of alkylated dienylmanganese tricarbonyl complexes. Considerable amounts of biphenyl were isolated from the reaction with phenyllithium, suggesting that electron transfer processes occur readily.

Treatment of **2a** with the lithium enolate **3** (generated from the silyl enol ether, by treatment with MeLi) in THF at 0°C (30 min) led to the isolation of a dienylmanganese tricarbonyl complex in 70% yield [6]. The $^1H$ NMR spectrum, showing unresolved multiplicity of the dienyl proton resonances, indicated the presence of two diastereoisomers, as expected, but only one regioisomer. However, it was not possible on this basis to determine unambiguously whether the structure of the product was **4** or **5**. That the correct structure was in fact **4** was shown conclusively by its conversion to the substituted aromatic compound **6** [6] using buffered ceric ammonium nitrate in acetone [7]. The 200 MHz $^1H$ NMR spectrum of **6** was exactly as anticipated for the substitution pattern shown [6].

The above method of preparation of arenemanganese tricarbonyl cations is applicable to other substituted derivatives. We have prepared the known [8] anisolemanganese tricarbonyl tetrafluoroborate **2b**, and the previously unprepared 4-bromoveratrole complex **2c** by this method, although the latter was obtained in somewhat lower yield (42%). The anisole complex underwent reaction with the cyclohexanone enolate **3** to give only the product **7** of *meta* addition (NMR) which could be converted to the *meta*-substituted anisole **8** by the above procedure (67% overall), but so far we have been unable to isolate characterisable adducts from similar reactions of **2c**. These procedures are therefore most




useful for complexes not carrying bromo substituents. It should be pointed out that reaction of (non-cyclic) ketone enolates with the unsubstituted benzene-manganese tricarbonyl hexafluorophosphate has previously been reported by Sweigart et al. [3] but we are unaware of any reports of similar reactions of the more complex alkoxy-substituted derivatives, which are more sensitive to the usual oxidation conditions.

Whilst it is known that MeO substituents on arenemanganese tricarbonyl com-

plexes deactivate *ortho* and *para* positions, leading to predominant nucleophilic attack at the *meta* position [2], the results described above demonstrate that the *para* position is in fact the most deactivated, leading to preferential addition of enolate nucleophiles at the sterically more hindered 3-position in complex 2a. An exactly analogous regioselectivity has been reported for the addition of $LiCR_2CN$ (R = H, Me) nucleophiles to veratrolechromium tricarbonyl [9] and this has been rationalized by correlation with arene LUMO coefficients [10]. We are not aware of any successful addition of ketone enolates to the chromium derivative, so we believe the more reactive manganese complex may be used in a complementary manner. Future work will be directed at exploring the range of substituted veratrole and related complexes available using $Mn(CO)_5BF_4$ and the types of nucleophile which react with these electronically deactivated systems.

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## References and notes

1 Reviews: G. Jaouen in H. Alper (Ed.), Transition Metal Organometallics in Organic Synthesis, Vol. 2, Academic Press, New York, 1978, Chapter 2; Ann. N.Y. Acad. Sci., 295 (1977) 59; M.F. Semmelhack, Tetrahedron, 37 (1981) 3956; Ann. N.Y. Acad. Sci., 295 (1977) 36; W.E. Silverthorn, Adv. Organomet. Chem., 13 (1975) 47.

2 P. Bachmann, K.-R. Repp and H. Singer, Z. Naturforsch. B, 32 (1977) 471; A. Mawby, P.J.C. Walker and R.J. Mawby, J. Organomet. Chem., 55 (1973) C39; G. Winkaus, L. Pratt and G. Wilkinson, J. Chem. Soc., (1961) 3807; P.J.C. Walker and R.J. Mawby, Inorg. Chem., 10 (1971) 404; Idem., Inorg. Chim. Acta, 7 (1973) 621; Idem., J. Chem. Soc., Dalton Trans., (1973) 622; R.J. Angelici and L.J. Blacik, Inorg. Chem., 11 (1972) 1754; P.L. Pauson and J.L. Segal, J. Chem. Soc. Dalton Trans., (1975) 1677, 1683; G.A.M. Munro and P.L. Pauson, Israel J. Chem., 15 (1976/77) 258; G.A.M. Munro and P.L. Pauson, J. Organomet. Chem., 160 (1978) 177.

3 Y.K. Chung, H.S. Choi, D.A. Sweigart and N.G. Connelly, J. Am. Chem. Soc., 104 (1982) 4245; Y.K. Chung, P.G. Willard, and D.A. Sweigart, Organometallics, 1 (1982) 1053.

4 G.A. Munro and P.L. Pauson, Z. Anorg. Allg. Chem., 458 (1979) 211.

5 Pauson has also shown that pentacarbonylmanganese perchlorate can be used for the preparation of arenemanganese tricarbonyl complexes: K.K. Bhasin, W.G. Balkeen and P.L. Pauson, J. Organomet. Chem., 204 (1981) C25.

6 All new compounds were characterized using infrared, $^1H$ NMR, and mass spectrometry or combustion analysis. Selected data are as follows **2**: IR ($cm^{-1}$, $CH_3CN$): 2080, 2018, 1290; $^1H$ NMR ($CD_3CN$): δ 6.09, br (2H, s), 6.21 br (2H, s), 3.98 (6H, s) ppm. **4** IR ($cm^{-1}$, $CHCl_3$): 2003, 1935, 1915, 1708, 1550; $^1H$ NMR ($CDCl_3$): δ 5.45 (1H, m, 3-H), 5.10 (1H, m, 4-H), 4.80 (1H, m, 5-H), 3.75 (3H, s, OMe), 3.55 (3H, s, OMe), 2.96 (1H, m, 6-H) 2.5—1.3 (9H, m) ppm. **6**: IR ($cm^{-1}$, $CCl_4$): 1716, 1604 (w), 1502 (w): $^1H$ NMR ($CDCl_3$): δ 7.06 (1H, t, *J* 8 Hz, 5-H), 6.85 (1H, d, *J* 8 Hz, 6-H or 4-H), 6.74 (1H, d, *J* 8 Hz, 4-H or 6-H), 3.98 (1H, dd, $J_{aa}$ 12 Hz, $J_{ae}$ 5 Hz, benzylic H) 3.86 (3H, s, OMe), 3.75 (3H, s, OMe), 2.5—1.6 (8H, m).

7 The procedure was as follows: Complex **4** (100 mg) and sodium acetate (200 mg) were stirred at room temperature in acetone (3 ml) while ceric ammonium nitrate (750 mg) was added in portions over a period of 6 h. Aqueous work-up and ether extraction, followed by preparative TLC on silica gel, afforded the product **6** in yields of 40—60%. Other methods of oxidative decomplexation (ref. 3) were unsuccessful.

8 P.L. Pauson and J.A. Segal, J. Chem. Soc. Dalton Trans., (1975) 1683.

9 M.F. Semmelhack and G. Clark, J. Am. Chem. Soc., 99 (1977) 1675.

10 M.F. Semmelhack, G.R. Clark, R. Farina and M. Saeman, J. Am. Chem. Soc., 101 (1979) 217.