Nucleophilic Addition to Coordinated Polyenes: A Novel Method for the Liberation of the Trimethylenemethane Ligand Involving C-C Bond Formation

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Abstract: Reaction of (trimethylenemethane)Fe(CO)₃ with carbon nucleophiles, followed by protonation yields the corresponding methallylated nucleophile in good yield. Products which incorporate carbonyl ligands are also observed.

There has been considerable recent interest in the application of acyclic diene(tricarbonyl)iron complexes to organic synthesis. The utility of these complexes is due to the ability of the bulky $Fe(CO)_3$ moiety to act as a protecting and stereodirecting adjunct.¹ Their ease of preparation from prochiral ligands and their resolution² into separate enantiomers have made these complexes of use in the preparation of chiral centers adjacent to a coordinated 1,3-diene. The diene ligand may be liberated in good yield by oxidation (eg. Ce⁴⁺) to generate the free diene³ or by photochemical reduction (hv, AcOH) to afford an olefin.⁴ Nucleophilic addition to the coordinated diene is reported to afford olefinic products.⁵



In contrast, application of isomeric (trimethylenemethane) $Fe(CO)_3$ complexes to organic synthesis is considerably more limited.⁶ While these complexes may be readily prepared,⁷ methodology for the liberation of the trimethylenemethane ligand (TMM) is somewhat limited. Treatment of the parent (TMM) $Fe(CO)_3$ complex 1a with Ce⁴⁺ in the presence of tetracyanoethylene generates methylenecyclopentane products in abysmally low isolated yield.⁸ Photochemical reduction of substituted (TMM) $Fe(CO)_3$ complexes has recently been reported to proceed in good isolated yield but with low regioselectivity.⁶ The reaction of complexes 1 with nucleophiles has not previously been reported.



The $(TMM)Fe(CO)_3$ complex is known to be "electron poor".⁹ In marked contrast to (butadiene)-Fe(CO)₃, Friedel-Crafts acylation of $(TMM)Fe(CO)_3$ proceeds in low yield.^{7b,10} For these reasons, it was envisioned that complexes 1 would be susceptible to attack by carbon nucleophiles.¹¹

The known complexes 1a, b, and c were prepared by reaction of the corresponding allylic dihalides with $Fe_2(CO)_9$.⁷ These were treated with carbon nucleophiles in THF/HPMA (4:1) followed by work-up with trifluoroacetic acid. The results are recorded in the Table. In most all cases, the corresponding allylated products could be isolated. However, the reaction of 1a with phenyl lithium predominantly gave products which incorporate a molecule of carbon monoxide, while the reaction of 1c under similar conditions merely produced isomeric (isoprene)Fe(CO)₃, 2.

These results are best accounted for by the following mechanism. Attack of the nucleophile at a terminal position of the TMM ligand generates an allyl-iron anion 3/4 which upon protonolysis affords the free ligand. A similar pathway has been proposed for the addition of nucleophiles to (diene)Fe(CO)₃ complexes.⁵ Alternatively, attack at coordinated CO may occur to afford a (TMM)acyl-iron anion 5. Such nucleophilic attack on coordinated CO by alkyl/aryl lithiums is known to occur for (diene)Fe(CO)₃⁵ and (enone)Fe(CO)₃¹². The acyl group is then transfered to the TMM ligand to afford an allyl-iron anion 6 in which the acyl oxygen can serve to coordinate to the iron metal. Subsequent protonolysis gives the product incorporating carbon monoxide. The isomerization of 1c to 2 might occur in the following fashion. Phenyl lithium acts as a base to deprotonate 1c to afford the cross-conjugated pentadienyl-iron anion 7. The formation of anion of this type have been previously reported.¹³ Protonation of the anion is reported to afford (methyl-TMM)Fe(CO)₃^{13b} which is known to rearrange to the thermodynamically more stable 2 under acidic conditions.^{7b}





TABLE. Reaction of Nucleophiles with (TMM)Fe(CO)₃ Complexes^a

^aWork-up: xs. CF₃COOH (-78°C, 1 h), followed by sat. aq. NaHCO₃ and extraction. ^b-78° to 23°C, 1.5 h. ^c-78°C, 1 h. ^dIdentified by comparison to literature spectral data. ^oRef. 14. ^fThis product contained a minor amount of inseparable 2-phenyl-1,3-dithiane. Hydrolysis of the mixture (HgCl₂, CdCO₃, H₂O) gave 3-methyl-1-phenyl-3-buten-1-one and 3-methyl-1-phenyl-2-buten-1-one (5:1).¹⁵ ^aRef. 15. ^hnew compounds, see Ref. 16. ⁱRef. 17. ^jRef. 18. ^k2,3-dimethyl-4,4-diphenyl-1-butene: Ref. 19, 3-methyl-5,5-diphenyl-2-pentene, Ref. 20. ^lRef. 13b.

In summary, a novel methodology for the liberation of the TMM ligand, involving C-C bond formation,

has been developed. The methodology presented here should broaden the synthetic potential of tricarbonyl-

(trimethylenemethane)iron complexes.

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12-methyl-1, s, s-mphenyl-1-balance. $b_{\rm H}$ (CDCl₃) 1.77 (d, J 1.2, 3H), 2.91 (d, J 7.8, 2H), 4.24 (t, J 7.8, 1H), 6.11 (br s, 1H), 6.9-7.8 (m, 15H); $\delta_{\rm C}$ (CDCl₃) 17.8, 46.6, 49.7, 125.8, 126.1, 127.6, 127.8, 128.0, 128.3, 128.7, 136.3, 138.3, 144.6; HRMS *m/z* 298.1720 (calcd for $C_{23}H_{22}$ *m/z* 298.1716).

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- 20. 3-methyl-5,5-diphenyl-2-pentene: (mixture of E and Z): $\delta_{\rm H}$ (CDCl₃) 1.35 (d, J 7.0) and 1.44 (d, J 7.0) total 3H, 1.55 (s) and 1.59 (s) total 3H, 2.76 (d, J 7.8) and 2.77 (d, J 7.8) total 2H, 4.11 (t, J 7.8) and 4.13 (m) total 1H, 5.07 (q, J 6.8) and 5.19 (q, J 6.6) total 1 H, 7.1-7.3 (m, 10H).

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