Preliminary Communication

Cationic arenetricarbonylmanganese complexes: addition of α-anionic Fischer type carbenes

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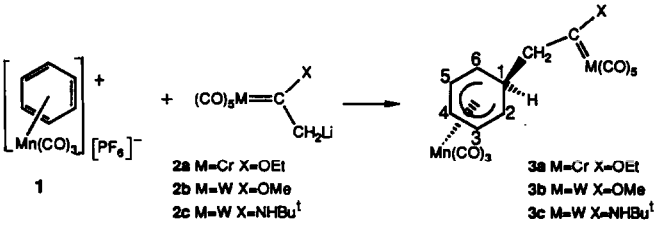
Abstract

The addition of $[(CO)_5M{=}C(OR)CH_2Li]$ (M = Cr or W) to $[(CO)_3Mn(C_6H_6)][PF_6]$ affords the dinuclear bridged complexes $[\mu\text{-}C(OR)CH_2)(\eta^5\text{-}C_6H_6)Mn(CO)_3\}\{M(CO)_5\}]$ (**3a** and **3b**), respectively; a similar reaction is observed with aminocarbene tungsten complex $[(CO)_5W{=}C(NHBu^t)(CH_2Li)]$.

Key words: Manganese; Chromium; Tungsten; Carbene; Addition; Carbonyl

Cationic (η^6-arene)tricarbonylmanganese complexes react easily with ketone enolates [1–3] giving neutral (η^5-cyclohexadienyl)tricarbonylmanganese derivatives. As ketone enolates and anionic Fischer-type carbenes have very close properties [4], we undertook the study of the Cr and W carbanions, **2a–c**, with cationic (η^6-arene)tricarbonylmanganese complexes. This communication reports the synthesis of new neutral dinuclear (cyclohexadienyl)tricarbonyl complexes obtained by the addition of α-anionic Fischer type carbenes to (η^6-benzene)tricarbonylmanganese cation.

Carbanion **2a**, prepared by treating the pentacarbonyl[(ethoxy)methylcarbene] [5] with ^{n}BuLi reacts with benzenetricarbonylmanganese hexafluorophosphate **1** [6] at −78°C to give the corresponding neutral manganese complex **3a*** (19% yield). In order to obtain a better yield, we undertook the experiment with the methoxymethyl(carbene)tungsten **2b** [5] and recovered complex **3b*** (62% yield after silica gel chromatography column and petroleum ether recrystallisation).



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2a M=Cr X=OEt
2b M=W X=OMe
2c M=W X=NHBu^t

3a M=Cr X=OEt
3b M=W X=OMe
3c M=W X=NHBu^t

We have also studied the reaction of anionic aminocarbene complex **2c** (prepared by treating the pentacarbonyl[(tert-butylamino)(methyl)(carbene)] tungsten [7] with ^{n}BuLi) with complex **1** which gives complex **3c** * (22% yield). These reactions are related to the additions of carbene carbanions to η^2, η^5 or η^7 complexes of other metals such as Re, Cr, Mo, and Fe [8,9]. We are now studying this reaction with substituted arenemanganese complexes, and with other carbene complexes.

The reaction of cationic arenetricarbonylmanganese complexes with anionic carbene complexes gives rise to a new class of dinuclear complex which has potential for organic and inorganic synthesis.

1. Experimental details

1.1. General procedure

A THF solution (10 ml) of pentacarbonyl[(methoxy)(methyl)carbene] tungsten (1 mmol) at −78°C under N_2 is treated by ^{n}BuLi (690 μl of a 1.6 M solution in hexane, 1.1 mmol). This solution is transferred by cannula to another flask containing a suspension of benzenetricarbonylmanganese hexafluorophosphate **1**

* Typical ^{1}H NMR data of tricarbonylcyclohexadienylmanganese complexes C_6D_6(ppm): **3a**: 0.88, 3H, t, J = 7, Me; 2.34, 2H, m, CH_2; 2.38, 2H m, H-2,6; 2.61, 1H, m, H-1; 4.04, 2H, t, J = 6, H-3,5; 4.44, 2H, q, J = 14 and 7, OCH_2; 4.93, 1H, t, J = 6, H-4. **3b**: 2.16, 2H, d, J = 7, CH_2; 2.34, 2H, t, J = 6, H-2.6; 2.59, 1H, m, H-1; 3.67, 3H, s, OMe; 4.04, 2H, t, J = 6, H-3,5; 4.93, 1H, tt, J = 6 and 1, H-4. **3c**: 0.59, 9H, s, ^{t}Bu; 1.79, 2H, d, J = 7, CH_2; 2.67, 2H, t, J = 6, H-2,6; 3.51, 1H, m, H-1; 4.04, 2H, t, J = 6, H-3,5; 4.85, 1H, t, J = 6, H-4; 8.51, 1H, s, br, NH. ^{13}C NMR C_6D_6 (ppm): **3a**: 14.7, Me; 33.3, C-1; 56.0, C-2,6; 75.5, CH_2; 78.2, OCH_2; 80.2, C-4; 96.6, C-3,5; 216.9 and 223.8, CrCO; 223.2, MnCO; 357.4, Cr=C. **3b**: 33.1, C-1; 55.7, C-2,6; 69.8, OMe; 76.8, CH_2; 79.9, C-4; 96.4, C-3,5; 197.3 and 203.4, WCO; 222.9, MnCO; 333.4, W=C. **3c**: 30.4, Me; 37.7, C-1; 56.4, C-2-6; 60.0, C^tBu; 60.7, CH_2; 78.8, C-4; 96.7, C-3,5; 199.8 and 203.2, WCO; 222.8, MnCO; 260.0, W=C. IR (cm^{-1}) (CCl_4): **3a**: 1940, 2025 $Cr(CO)_5$, 1940, 2005 $Mn(CO)_3$; **3b**: 1940, 1975, 2030 $W(CO)_5$, 1940, 2005 $Mn(CO)_3$; **3c**: 1925, 2055 $W(CO)_5$, 1925, 2010 $Mn(CO)_3$.

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(1 mmol) in dry THF (5 ml) at −78°C. After 3 min, ether (30 ml) and water (20 ml) are introduced into the flask. After extraction with ether and evaporation of the organic solvents under reduced pressure, a crude oil is obtained which was purified by silica gel chromatography (petroleum ether) and recrystallized from petroleum ether giving **3b** (62% yield). The spectroscopic data of **3b** can be compared with those of η^5-cyclohexadienyl complexes obtained by addition of organic nucleophiles [10]. Satisfactory spectral and mass spectra data have been obtained for all new compounds.

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