Reactions of Cyclopentadienyl Metal Carbonyl Anions with the 1,2,3-Tri-t-butylcyclopropenium Cation; Electrophilic Attack at Peripheral Ligands

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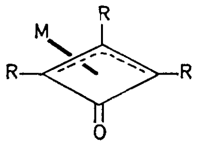
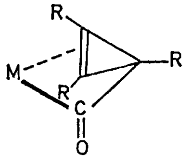
Summary The $[(\eta^5\text{-}C_5H_5)M(CO)_n]^-$ anions (M = Fe, $n = 2$; M = Mo, W, $n = 3$) react with the tri-t-butylcyclopropenium cation to give organometallic products derived from electrophilic attack on ligands rather than at the metal; the first examples of electrophilic attack of the $\eta^5\text{-}C_5H_5$ ring in a cyclopentadienyl Group VI metal carbonyl are reported.

Reactions of substituted cyclopropenium cations with metal carbonyl anions have been remarkably unsuccessful in the preparation of η^3-cyclopropenyl metal systems,[1] although such species have been generated by other routes.[2–4] Notably reactions of $[(\eta^5\text{-}C_5H_5)M(CO)_n]^-$ anions (M = Fe, $n = 2$; M = Mo, $n = 3$) with the triphenyl- and trimethylcyclopropenium cations (**1a**) and (**1b**) do not yield organometallic derivatives incorporating the three-membered ring.[1] Very low yields (*ca.* 2%) of the cyclobutenyl complex (**2a**) were obtained from the reaction of $[Co(CO)_4]^-Na^+$ with (**1b**)[5]; this reaction was an extension of the original work by Coffey[6] on the reaction of triphenylcyclopropenyl bromide with $Co(CO)_4^-$ and $Fe(CO)_3NO^-$ to yield the analogous complexes (**2b**) and (**2c**). An alternative structure (**3a**)[6] for these complexes was discounted after an *X*-ray diffraction study confirmed the structure of (**2b**).[7]

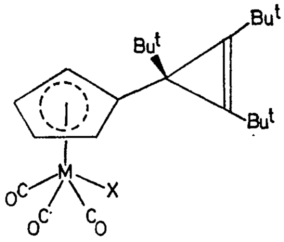
In agreement with previous observations,[1] we have found that the reactions of $[(\eta^5\text{-}C_5H_5)M(CO)_n]^-$ anions (M = Fe, $n = 2$; M = Mo, W, $n = 3$), as their Na^+ salts, with the di-t-butylmethylcyclopropenium cation (**1c**) (tetrahydrofuran; 20 °C) gives virtually quantitative yields of the corresponding organometallic dimers $[(\eta^5\text{-}C_5H_5)M(CO)_n]_2$ (M = Fe, $n = 2$; M = Mo, W, $n = 3$), together with a mixture of organic compounds, shown by mass spectrometry to be dimers of empirical formula $(Bu^t_2MeC_3)_2$. Similar observations have been made in the reaction of $[Mn(CO)_5]^-$ with the tropylium cation, affording only $[Mn_2(CO)_{10}]$ and bitropyl.[8]



(2a) M = Co(CO)$_3$; R = Me
(2b) M = Co(CO)$_3$, R = Ph
(2c) M = Fe(CO)$_2$NO; R = Ph
(4) M = $(\eta^5\text{-}C_5H_5)$Fe(CO); R = Bu^t



(3a) M = Co(CO)$_3$; R = Ph
(3b) M = $(\eta^5\text{-}C_5H_5)$Fe(CO); R = Bu^t



(5a) M = Mo, X = H
(5b) M = W, X = H
(5c) M = Mo, X = Cl
(5d) M = W, X = Cl

In contrast, the analogous reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-$ with $[C_3Bu^t_3]^+BF_4^-$ (**1d**) gave only low yields of $[\{(\eta^5\text{-}C_5H_5)Fe(CO)_2\}_2]$, the major product (70%) being the orange-yellow crystalline complex [(**4**), m.p. 69—71 °C (decomp.); ν_{CO}(hexane) 1978s, and 1708m cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) at τ 5·12 (5H, s), 8·45 (9H, s), and 8·73 (18H, s); *m/e* 384 (M^+)]. The medium intensity i.r. band at 1708 cm^{-1} is characteristic of the oxocyclobutenyl ligand.[5]

In further contrast, the corresponding reactions of the $[(\eta^5\text{-}C_5H_5)M(CO)_3]^-$ anions (M = Mo, W) with (**1d**) exhibited no propensity towards oxocyclobutenyl ligand formation, or formation of a metal–carbon σ-bonded complex. Almost quantitative yields of air-sensitive, pale yellow crystals of the hydrido-complexes (**5a**) [m.p. 57—60 °C (decomp.); ν_{CO}(hexane) 2014s and 1930brs cm^{-1}, ^{1}H n.m.r. (C$_6$D$_6$) at τ 5·03 (2H, t, J 2 Hz), 5·41 (2H, t, J 2 Hz), 8·81 (18H, s), 9·09 (9H, s), and 15·04 (1H, s)] and (**5b**) [m.p. 91—93 °C (decomp.); ν_{CO}(hexane) 2018s and 1928br,s cm^{-1}; ^{1}H n.m.r. (C$_6$D$_6$) at τ 5·01 (2H, t, J 2 Hz), 5·45 (2H, t, J 2 Hz), 8·81 (18H, s), 9·91 (9H, s), and 17·82 (1H, t, J_{W-H} 37 Hz); *m/e* 540 (M^+)] were obtained. Complexes (**5a**) and (**5b**) reacted rapidly with CCl$_4$ to afford the corresponding air-stable, orange complexes [(**5c**), ν_{CO}(CCl$_4$) 2052s, 1976s, and 1956m cm^{-1}] and [(**5d**); ν_{CO}(CCl$_4$) 2044s, 1958s, and 1940m cm^{-1}].†

These reactions represent the first examples of electrophilic substitution of a cyclopentadienyl ring in cyclopentadienyl derivatives of the Group VI metal carbonyls. *exo*-Attack on the cyclopentadienyl ring is implied, the resultant *endo*-hydrogen undergoing a proton shift to the metal. Examples of electrophilic substitution in electron-rich benzene derivatives by the triphenylcyclopropenium cation have been described.[9]

The propensity of cyclopropenium cations towards a one-electron reduction to the corresponding radicals is well established.[10] Furthermore, dimerisation of the resultant radicals to yield bicyclopropenyl compounds, which may then rearrange further, is very fast.[10] Thus, a one-electron transfer reaction must be the lowest energy reaction pathway available in the reactions of (**1a**), (**1b**), and (**1c**) with metal carbonyl anions; metal–carbon bond formation is apparently not favoured.‡ Such a process must require the anionic metal centre and the cation to attain some proximity to one another for the electron transfer to occur.[10] Approach to the metal centre must therefore be sterically precluded in the reactions of (**1d**), the cation being forced along less sterically demanding reaction pathways, involving attack at peripheral sites.

This hypothesis demands that the oxocyclobutenyl ligand in (**4**) be formed by electrophilic attack of (**1d**) on a co-ordinated CO ligand, affording an intermediate (**3b**) which undergoes ring expansion to yield (**4**); generation of (**3b**) cannot occur *via* initial formation of a metal-carbon bond followed by CO insertion.

The stereoselectivity of attack by $Bu^t_3C_3^+$ at either the $\eta^5\text{-}C_5H_5$ ring or at CO, with variation of the metal, is remarkable, since it is difficult to visualise any steric reasons. Such selectivity may therefore imply significant differences in electron density distribution at different ligand sites in the various anions.

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† Satisfactory microanalyses have been obtained for all complexes.

‡ That this is not due to the intermediate formation of some inherently unstable metal–carbon bond is shown by the generation of a stable η^3-cyclopropenyl–molybdenum bond by an alternative route (ref. 3).

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