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NEW IRON COMPLEXES FROM NUCLEOPHILE ADDITION/ CARBONYLATION OF η^4-(1,3-DIENE)TRICARBONYLIRON(0) COMPLEXES

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Summary

A series of novel organoiron complexes has been isolated and studied by ^1H NMR, ^{13}C NMR, and IR spectroscopy. Addition of $LiC(CH_3)_2CN$ to (1,3-cyclohexadiene)tricarbonyliron produces an intermediate which is only stable at low temperature and which is assigned the homoallyl—$Fe(CO)_3$ anion structure. The intermediate rearranges on warming into a stable complex, for which full spectral data support the structure as an allyl—$Fe(CO)_3$ anionic species. Interception of the first formed intermediate with CO gives an acylferrate complex with an olefin unit still bound to iron, and methylation then occurs at oxygen to produce an unusual internally-bound (alkene)(methoxyalkylidene)tricarbonyliron species.

A series of reactive carbon nucleophiles has been reported to add to η^4-(1,3-diene)tricarbonyliron(0) complexes (e.g., 1) [1]. Two intermediates (**2**, **3**) are the likely products. Quenching of the mixture with acid produces substituted cyclohexenes, which could result from either 2 or 3 [1]. Reaction in the presence of CO appears to lead to a new intermediate, suggested to be 4 [2]. The structure 4 is an analog of the well-studied acyltetracarbonylferrates [3]; consistent with this formulation, reaction with acid produces a 1-formyl-3-cyclohexene derivative, while reaction with methyl iodide produces a 1-acetyl-3-cyclohexene [2]. However, reaction with methyl fluorosulfonate produces a new intermediate (now formulated as 5) which is converted to a 1-carbomethoxy-3-cyclohexene derivative when handled in air [2,4]. Under certain conditions, the first-formed intermediate (2) rearranges to a new species (now formulated as 3) which does not undergo CO insertion under moderate CO pressure [2]. In this paper, we describe efforts to characterize the novel intermediates 2—5 through spectral data.

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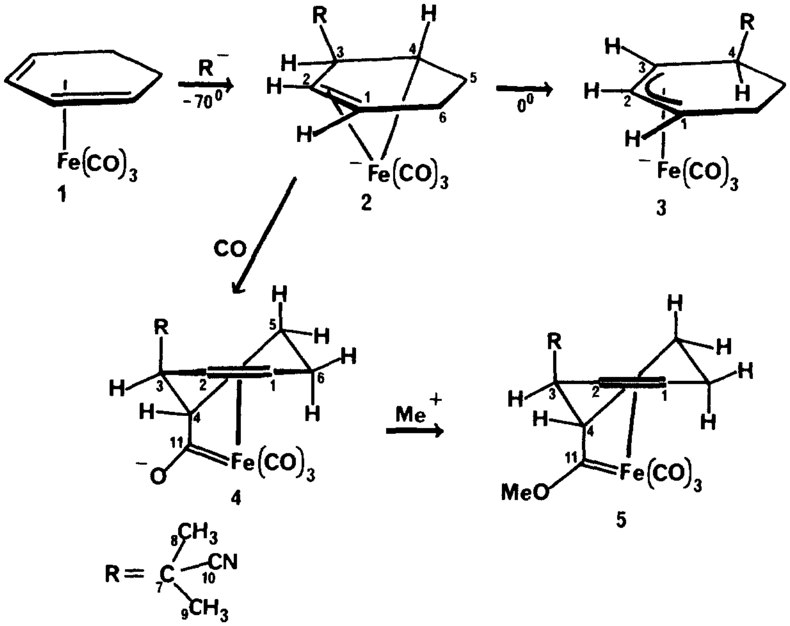
Reaction of $LiC(CH_3)_2CN$ with 1 at -60°C in THF-d_8 produced a mixture which exhibited a poorly resolved ^1H NMR spectrum. Peaks for 1 and 3 were clearly absent, and two well-defined signals at δ 3.20 and 3.71 are assigned to the olefinic protons in 2 [5]. As the solution was allowed to warm to 0°C, the pattern changed and sharpened into a spectrum attributed to 3, with excellent resolution.



The ^1H NMR spectrum of η^3-allyl complex 3 exhibits a triplet at δ 5.12 (J 5.6 Hz) assigned to H at C(2), and two narrow multiplets, centered at δ 3.60 and 3.43 (approximately a doublet with $J \cong$ 6 Hz), assigned to H at C(1) and C(3) [6]. Irradiation at δ 3.5 caused the triplet at δ 5.12 to collapse to a sharp singlet, while irradiation at δ 5.12 changed the signals for H at C(1) and C(3) into broad singlets, suggesting small residual coupling with H at C(4) and C(6). Irradiation in the region assigned to H at C(4) and C(6) (δ 2.2) simplified the signals from H at C(1) and C(3) into sharp doublets with J 5;6 Hz. Three doublets in the ^{13}C NMR spectrum at δ 68.2, 54.4, and 57.2 are assigned to C(2) and C(1) or C(3), respectively [6]. The IR spectrum shows metal-bound CO at 1926, 1843, and 1826 cm^{-1}, indicating increased back-bonding relative to the starting complex [7].

When addition of $LiC(CH_3)_2CN$ to 1 was made under 1.5 atm of CO at -60°C in THF, a stable compound was obtained whose structure was assigned as 4. The IR spectrum shows terminal Fe—CO signals at 1971 and 1875 cm^{-1}, while the acyl CO is assigned to the peak at 1591 cm^{-1} [8]. The ^1H NMR spectrum includes two doublets of narrow multiplets centered at δ 4.20 and 3.44 assigned to H at C(2) and C(1), respectively (olefinic H). Irradiation in the region δ 2.0—2.8 simplifies these signals to sharp doublets with J 8.1 Hz. A triplet appears at δ 2.42, J 4.9 Hz, assigned to H at C(3); it collapses to a doublet during irradiation at δ 4.20, suggesting a coupling constant of 4.9 Hz between H at C(2) and H at

C(3). The magnitude of this coupling constant is consistent with a dihedral angle of 46° between C(2)-H and C(3)-H [9]. Molecular models of 4 show that this angle is consistent with either a *cis* arrangement of a pseudo-equatorial isobutyronitrile unit and the acyl group, or a *trans*-arrangement with the isobutyronitrile unit in a pseudo-axial conformation. The latter formulation (as represented by 4) is consistent with the *trans*-3,4-disubstituted cyclohexenes obtained after acid cleavage or reaction with MeI [2]. The ^{13}C NMR spectrum of 4 is notable for two doublets, at δ 58.1 and 50.2 assigned to C(1)/C(2), and a singlet at δ 300.1 assigned to the acyl carbon, C(11) [10]. The strong downfield position of the signal for C(11) is consistent with a major contribution from resonance structure 4, emphasizing the alkylidene structure [11].

Treatment of the solution of 4 with methyl fluorosulfonate gives a new intermediate, 5, which can be isolated as an orange oil and fully characterized. Significant peaks appear in the IR spectrum at 2024, 1957, and 1922 cm^{-1} (terminal Fe—CO), at 1697 cm^{-1} due to Fe=C(OMe)R, and at 1266 cm^{-1} (C—O single bond stretch). The ^{1}H NMR spectrum exhibits a singlet at δ 4.08 for the OCH_3 group, and two doublets of narrow multiplets (δ 4.54, 4.27) assigned to the olefinic C-H (H at C(1), C(2)). The olefinic signals are substantially downfield in this neutral complex, compared to the corresponding signals in the anionic complex 4, consistent with less backbonding from iron to the alkene ligand in 5 [11]. Similarly, C(1) and C(2) in 5 give rise to doublets at δ 69.5 and 65.9. The alkylidene carbon C(11)) appears as a singlet at δ 341.7, comparable to data from other "Fischer-type" alkylidene complexes [12].

We feel these data establish the structures of previously postulated intermediates; especially significant is the conclusion that the alkene unit is still bound to iron in 4 and 5, ruling out displacement of the alkene by CO under these conditions. Important questions about the mechanisms of rearrangement 2→3 are still open.

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Full spectral data on 4: ^{1}H NMR (acetone-d_6, 250 MHz): δ 4.20 (dm, 1 H, J 8.1 Hz, H at C(2)); 3.43 (dm, 1 H, J 8.1 Hz, H at C(1)); 2.63 (m, 1 H, H at C(4)); 2.42 (t, 1H, J 4.9 Hz, H at C(3)); 2.36 and 1.89 (2 sets of m, H at C(6)); 1.80 and 1.31 (2 sets of m, H at C(5)). Irradiate δ 2.3—2.7; 4.20 (d, J 8.1 Hz); 3.43 (d, J 8.1 Hz). Irradiate δ 4.20: 2.42 (d, J 4.9 Hz). ^{13}C NMR (acetone-d_6): δ 300.0 (S, C(11)); 220.0 (s, C(12)); 210.1 (s, C(12)); 124.8 (s, C(10)); 58.7, 56.9 (2d, C(3,4)); 58.1, 50.2 (2d, C(1,2)); 34.9 (s, C(7)); 27.1, 25.8 (2t, C(5,6)); 23.4, 21.1 (2q, C(8,9)). IR (4/1 benzene-d_6/DMSO-d_6) 1971, 1875 (s, C≡O); 1591 (s, C—O) cm^{-1}.

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Full spectral data on 5: ^{1}H NMR (benzene-d_6, 80 MHz): δ 4.54 (dm, 1 H, J 8.0 Hz, H at C(2)); 4.17 (dm, 1H, J 8.0 Hz, H at C(1)); 4.08 (s, 3H, OCH$_3$); 2.5—2.9 (m, 2H, H at C(3,4)); 1.6—2.3 (m, 4H, H at C(5,6)); 0.95, 0.73 (2s, 6H, H at C(8,9)). ^{13}C NMR (benzene-d_6): δ 341.7 (s, C(11)); 216.2 (s, C(12)); 209.7 (s, C(12)); 123.6 (s, C(10)); 74.7 (q, OCH$_3$); 69.5, 65.9 (2d, C(1,2)); 56.1, 50.4 (2d, C(3,4)); 35.0 (s, C(7)); 27.1, 25.4 (2q, C(8,9)); 23.3, 22.8 (2t, C(5,6)). IR (benzene-d_6); 2024, 1957, 1922 (s, C≡O); 1697 (s, carbene C—O); 1266 (s, OCH$_3$) cm^{-1}. Mass spectrum (EI): 331 (M, 23); 303 (7.9); 275 (9.7); 247 (51.1); 148 (27.2); 123 (83.0); 91 (100). Mass spectral mol. wt.: calcd. for $C_{15}H_{17}FeNO_4$ 331.0507; found 331.0503.