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ON THE STABILITY AND LABILITY OF A DIENEIRON TRICARBONYL COMPLEX

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Summary

The ^{1}H and ^{13}C NMR spectra of (1-methoxy-1,3-cyclohexadiene)iron tricarbonyl have been reinvestigated. Determination of the ^1J(CH) coupling constants and the energy barrier for basal—apical CO ligand exchange makes possible the discussion of the stability and lability of the complex in terms of electronic perturbations.

In the course of our work on iron carbonyl complexes [1, 2], we have reinvestigated the ^{1}H and ^{13}C NMR spectra of (1-methoxy-1,3-cyclohexadiene)-iron tricarbonyl [3]. The carbon chemical shifts differ somewhat from those reported earlier [4] ($CDCl_3$ solution, δ in ppm from internal TMS, ±0.1 ppm): 212.0 (CO ligands), 116.9 (C-1), 78.2 (C-2), 77.2 (C-3), 58.0 (C-4), 56.0 (OCH_3), 25.1 and 23.2 (C-5 and C-6). Using the novel "Gated Spin Tickling" procedure [5], we have obtained values of the ^1J(CH) coupling constants (±2 Hz) which confirm our chemical shift assignments: ^1J = 175 (C-2, d); 175 (C-3, d); 162 (C-4, d); 145 (C-7, q); 135 (C-5, t); and 135 (C-6, t).

The magnitude of the ^1J(CH) coupling constants at C-2, C-3 and C-4 indicates essentially trigonal hybridization of the corresponding centers, and is thus favouring a predominant π-complex formulation [6]. Noteworthy is the observation of an increase in the ^1J(CH) values at the intermediate carbons (C-2 and C-3), relative to the terminal carbon (C-4); taken together with the above chemical shifts, it implies greater electronic depletion at C-2 and C-3 upon formation of the π-complex. Furthermore, the virtual equality of the chemical shifts at C-2 and C-3 as well as of the corresponding ^1J(CH) coupling constants point to very similar charge distributions at these two positions. Likewise, the proton chemical shifts at C-2 and C-3 are very similar, δ = 5.35 and 5.1 respectively. In contrast, our INDO [7] calculation gives total electronic charges (*me*) of −80, +40 and −20 at C-2, C-3 and C-4 of the parent 1-methoxy-1,3-cyclohexadiene, which must therefore involve a substantial amount of polarization from the electron-releasing methoxy substituent. The equalization of the charge densities at C-2 and C-3 in the organometallic compound is an interesting phenomenon.

Another puzzling result is the magnitude of the energy barrier for basal—apical CO ligand exchange. The ^{13}C carbonyl signals coalesce at 212 K, with slow exchange chemical shifts of 206.9 and 216.2 ppm for the two basal and for the apical CO ligands, respectively. The complete line shape analysis with the Saunders program [8] yields a value $\Delta G_c^{\neq}$ = 7.3 ± 0.2 Kcal mol^{-1}, virtually undistinguishable from that observed for (1,3-hexadiene)iron tricarbonyl [9]. Thus, making the diene a better donor *and* a better acceptor towards back-donation from the metal (since introduction of the methoxy group shifts both the HOMO and the LUMO by ca. 0.8 eV from the INDO calculation) has a mutually-cancelling effect, and the overall lability is little affected. Finally, the chemical shift reported here for the basal CO ligands, viz. 206.9 ppm, is among the highest for diene—$Fe(CO)_3$ complexes.

Experimental

The compound (π-$CH_3OC_6H_7$)$Fe(CO)_3$ was prepared as previously described [3] and purified by repeated elutions on a neutral alumina column under argon. ^{1}H NMR spectra were determined on a Varian T60 instrument. ^{13}C NMR spectra were determined on a Bruker HFX90 instrument.

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