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Variable Temperature Circular Dichroism of Tricarbonyl(1,3-diene)iron Complexes

CHARLES BARRAS, RAYMOND ROULET*

Institute of Inorganic and Analytical Chemistry, University of Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland

and PIERRE VOGEL*

Institute of Organic Chemistry, University of Lausanne, Rue de la Barre 2, CH-1005 Lausanne, Switzerland

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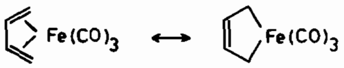
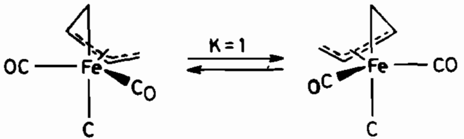
In the crystalline state, X-ray crystallographic analysis of tricarbonyl(1,3-diene)iron complexes has established that the coordination polyhedron of the iron atom is tetragonal pyramidal with one apical CO; the diene is perpendicular to the basal plane with three statistically equal C–C distances and two equal Fe–C(terminal) distances [1]. Hence, the two valence bond representations I–I′ have been widely used to describe the iron–diene interaction [2].

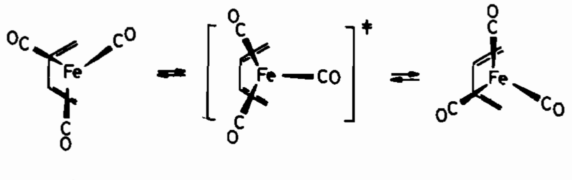


I I'

Recently, several arguments have been advanced [3] for a representation II ⇄ III (hypothesis A) involving an equilibrium between a pair of rapidly interconverting enantiomers having a σ-alkyl, η^3-allyl bonding mode. An alternative, hypothesis B, which also involves two rapidly interconverting enantiomeric structures would be an equilibrium between species IV ⇄ V (possibly *via* a C_s symmetrical transition state).

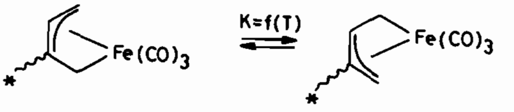


II III



IV (C_1) C_s V (C_1)

In principle, unequal Fe–C(diene) distances are expected in C_1 species II–V. Unequal Ni–C(terminal) distances have recently been observed in the crystal structure of a (1,3-diene)nickel complex [4], whereas in comparable iron complexes such asymmetrical bonding of the diene ligand has not yet been detected in the solid state [1, 2]. However, in the gas phase or in solution, hypotheses A or B have not yet been ruled out for (1,3-diene)Fe(CO)$_3$ complexes. In order to test the validity of these hypotheses which, at the limit, could be two different representations of the same equilibrium, we prepared optically pure complexes (–)-X, (+)-X, (–)-XII, (–)-XIII and (+)-XIV (Scheme 1). As the 2-substituted 5,6-dimethylidenebicyclo[2.2.1]heptane ligand in these complexes is itself chiral, the hypothetical equilibria II ⇄ III or IV ⇄ V would involve pairs of diastereoisomers (*e.g.* VI ⇄ VII). The equilibrium constants, K, for these equilibria should therefore be different from unity and should vary with temperature. Since the hypothetical pairs of chromophores II ⇄ III or IV ⇄ V have opposite chirality, variable temperature circular dichroism should be a suitable method to detect the existence of such equilibria.



VI VII

The choice of the bicyclo[2.2.1]heptane ligands was based on the following considerations: (*i*), the rigid bicyclic skeleton should minimize ligand conformational problems, (*ii*), isomeric complexes can be obtained (*exo* and *endo* metal coordination), and (*iii*), a remote substituent at C(2) is expected to cause only a minor perturbation of the (diene)-Fe(CO)$_3$ moiety. Consequently, the equilibrium constant K will remain *ca.* 1 which is a necessary condition to detect a change in K over the temperature range 77–300 K. (*iv*) The nature of the substituent can be varied widely. Hence, complexes that are soluble in both polar and unpolar solvents and give transparent glasses at 77 K can be obtained.

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*Authors to whom correspondence should be addressed.

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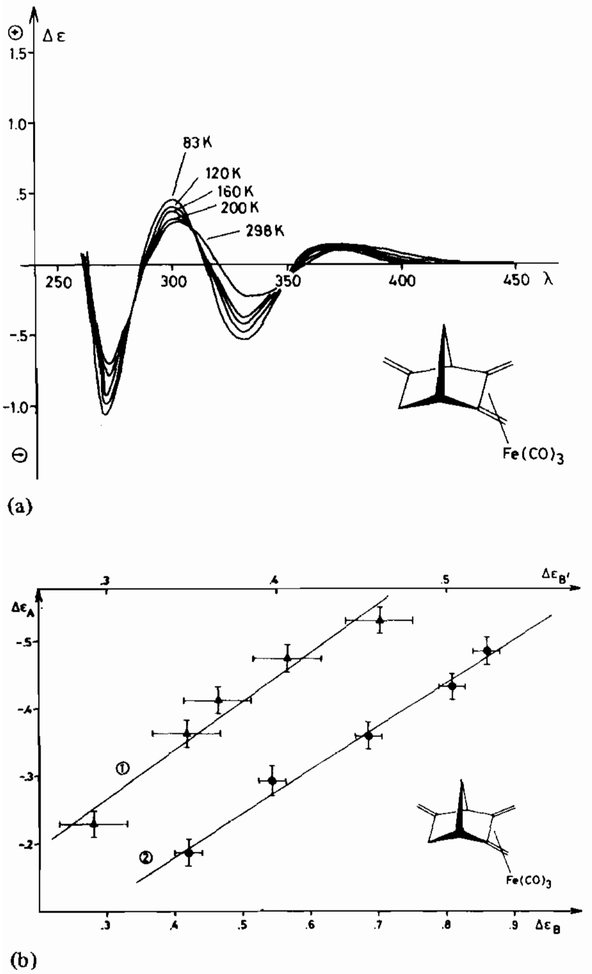
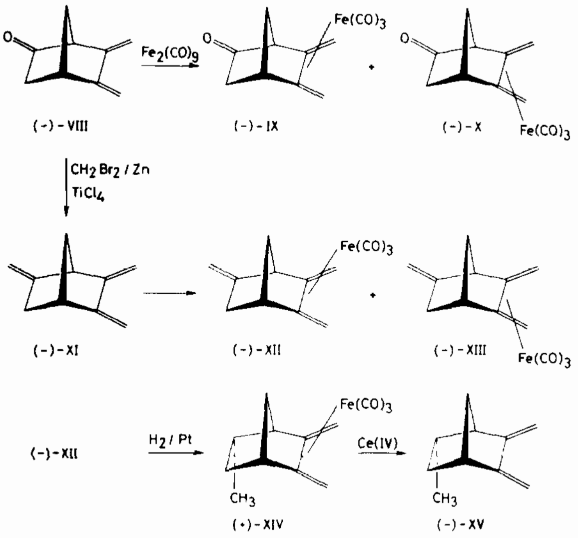


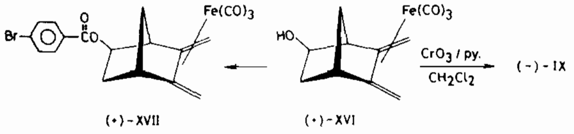
Fig. 1. Variable temperature CD spectra of (−)-tricarbonyl-([C,8,9,C-η]-2,3,5-trimethylidenebicyclo[2.2.1]heptane)-iron(*endo*) (−)-XIII in isopentane/methylcyclohexane 3:1, and plot of $\Delta\epsilon_A(T)$ *vs.* $\Delta\epsilon_B(T)$ (λ_A = 335; λ_B = 305 nm) in methanol/2-methyltetrahydrofurane 1:2 (1) and isopentane/methylcyclohexane 3:1 (2).

When treated with $Fe_2(CO)_9$ in methanol, the known (−)-(1S)-5,6-dimethylidene-2-bicyclo[2.2.1]-heptanone (−)-VIII [5] yielded a 2:1 mixture of the *exo* and *endo* complexes (−)-IX (44%) and (−)-X (22%), respectively.



Only the latter complex could be obtained in the pure state as a crystalline substance (m.p. 94–95 °C; $[\alpha]_D^{25}$ = −63.6°, c = 13 g/l, $CHCl_3$). Following Nozaki's technique [6] applied by Schwager [7] to the preparation of the racemic 2,3,5-trimethylidenebicyclo[2.2.1]heptane, the optically pure triene (−)-XI (colorless liquid; $[\alpha]_D^{25}$ = −63.9°, c = 49 g/l, $CHCl_3$) was obtained from (−)-VIII. When treated with $Fe_2(CO)_9$ in methanol, it gave a 2:1 mixture of complexes (−)-XII (18%; $[\alpha]_D^{25}$ = −45.6°, c = 11 g/l, $CHCl_3$) and (−)-XIII (8%; $[\alpha]_D^{25}$ = −89.9°, c = 0.9 g/l, isopentane/methylcyclohexane 3:1). These two complexes could be separated by HPLC [8] and isolated in a pure state as yellow liquids. Catalytic hydrogenation of (−)-XII afforded (+)-XIV (96%, yellow liquid; $[\alpha]_D^{25}$ = +24.1°, c = 8 g/l, $CHCl_3$). Oxidation of (+)-XIV with $(NH_4)_2Ce(NO_3)_6$ in acetone gave the uncomplexed diene (−)-XV (90%, colourless oil; $[\alpha]_D^{25}$ = −37.3°, c = 8 g/l, $CHCl_3$).

The absolute configuration of these new compounds was obtained by chemical correlation with the known alcohol (+)-XVI. The absolute configuration of the corresponding parabromobenzoate derivative (+)-(1S,2R)-XVII was established by X-ray crystallography [9]. The *exo* position of the iron atom in (−)-XII was confirmed by direct methylenation of (−)-IX. The *endo* position of the methyl group in (+)-XIV and (−)-XV was established by ¹H NMR spectroscopy [9].



The CD spectra of (−)-X (and (+)-X, prepared from (+)-VIII), (−)-XII (Fig. 1), (−)-XIII (Fig. 2), (+)-XIV and (+)-XVI were measured in isopentane/methylcyclohexane 3:1 and in methanol/2-methyltetrahydrofurane 1:2. The spectra obtained from these complexes were all temperature dependent, whereas those obtained from the uncomplexed ligands (−)-XI and (−)-XV in the same solvents were temperature *independent* between 77 and 295 K. For (−)-X, (+)-X and (+)-XVI, plots of $\Delta\epsilon_A(T)$ *vs.* $\Delta\epsilon_B(T)$ (A and B represent the maximum and minimum of the dichroic curve, respectively) were

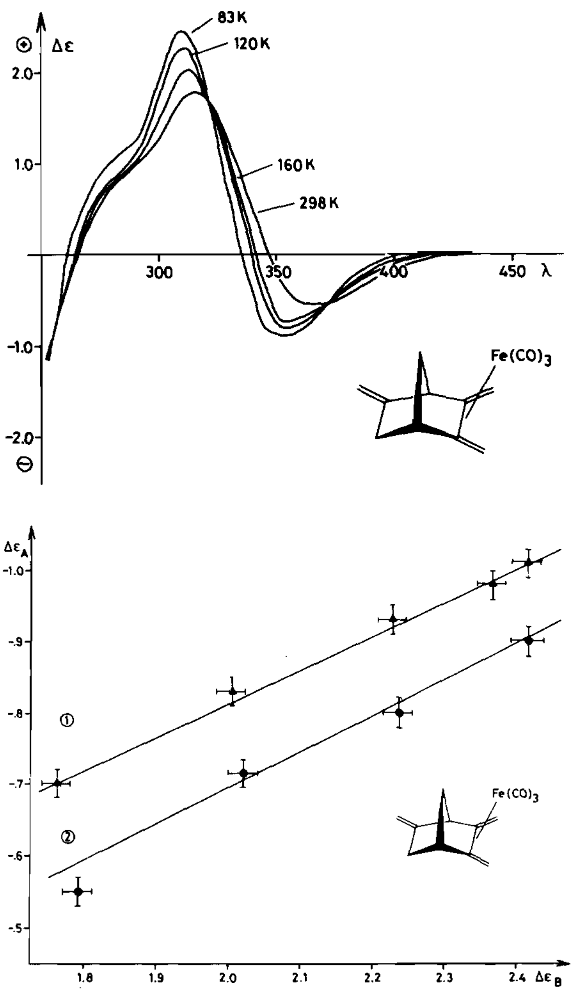


Fig. 2. Variable temperature CD spectra of (–)-tricarbonyl-([C,8,9,C-η]-2,3,5-trimethylidenebicyclo[2.2.1]heptane)iron (*exo*) (–)-XII in isopentane/methylcyclohexane 3:1, and plot of $\Delta\epsilon_A(T)$ *vs.* $\Delta\epsilon_B(T)$ (λ_A = 365; λ_B = 315 nm) in methanol/2-methyltetrahydrofurane 1:2 (1) and isopentane/methylcyclohexane 3:1 (2).

not linear. This indicates that solvent effects and/or solute aggregation are partly or totally responsible for the observed temperature-dependent CD spectra. However, for the least polar systems (–)-XII, (–)-XIII and (+)-XIV, linear plots of $\Delta\epsilon_A(T)$ *vs.* $\Delta\epsilon_B(T)$ were obtained in both the polar and apolar solvents (see *e.g.* Fig. 1). Furthermore, isodichroic points were observed between 77 and 298 K for these complexes in the two above-mentioned solvents.

The CD results obtained for (–)-XII, (–)-XIII and (+)-XIV are consistent with the existence of equilibria between pairs of rapidly interconverting diastereoisomers. Therefore, they are consistent with either hypothesis A or B. We thus suggest that the σ-alkyl, η^3-allyl bonding mode is a plausible representation for tricarbonyl(1,3-diene)iron complexes in the gas phase and in solution.

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