Journal of Organometallic Chemistry, 319 (1987) C45–C50
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

PHOSPHINE-CENTRED RESOLUTION OF (η^4-diene)Fe(CO)$_3$ COMPLEXES: (η^4-tropone)Fe(CO)$_2$L AND (η^4-isoprene)Fe(CO)$_2$L [L = (+)-(neomenthyl)PPh$_2$]

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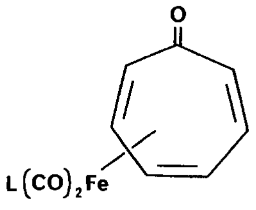
(Received September 22nd, 1986)

Summary

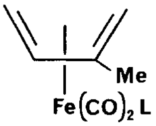
(η^4-Tropone)Fe(CO)$_3$ and (η^4-isoprene)Fe(CO)$_3$ form separable diastereoisomers on substitution of CO by (+)-(neomenthyl)PPh$_2$. In the tropone complex, diastereoisomer interconversion occurs by a 1,3-metal shift. The absolute configuration of the isoprene complex has been determined crystallographically.

The use of chiral cyclic and acyclic (η^4-diene)Fe(CO)$_3$ and [(η^5-dienyl)Fe(CO)$_3$]$^+$ complexes in asymmetric organic synthesis [1] is hampered by a lack of general routes to fully resolved complexes. Reported methods, which are diene- or dienyl-centred, limit the range of fully resolved complexes either to substituted [(cyclohexadienyl)Fe(CO)$_3$]$^+$ salts, and their derived (cyclohexadiene)Fe(CO)$_3$ counterparts [2], or to cyclic or acyclic (diene)Fe(CO)$_3$ complexes containing diene substituents (e.g. COOH, CHO) which are amenable to resolution by classical organic



(1) L = CO

(3) L = (+) - (neomenthyl) PPh$_2$



(2) L = CO

(4) L = (+) - (neomenthyl) PPh$_2$

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procedures [3]. We wish to report here a potentially general method based on metal-bound chiral phosphines, and its application to the resolution of (η^4-tropone)Fe(CO)$_3$ (**1**) and (η^4-isoprene)Fe(CO)$_3$ (**2**), complexes which are not amenable to resolution using presently available methods.

Complex **1** may be taken as an example of asymmetry residing in the η^4-coordi-

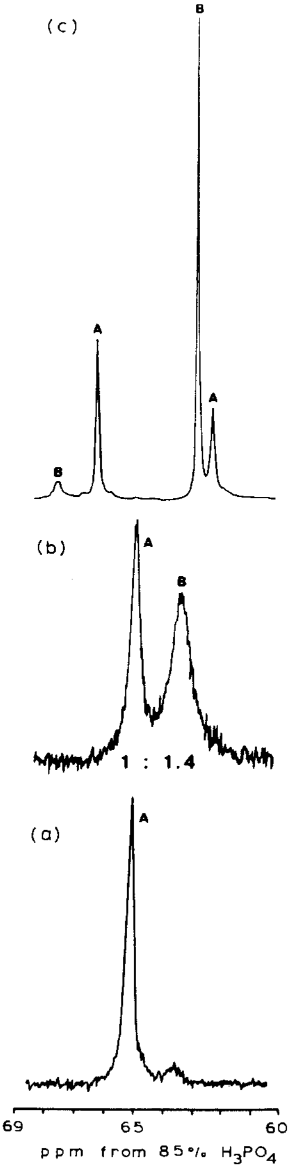

Fig. 1. Variable temperature ^{31}P NMR spectra of (tropone)Fe(CO)$_2$L (L = (+)-(neomenthyl)PPh$_2$) (CD$_2$Cl$_2$); (a) pure diastereoisomer (A) at 0°C, (b) equilibrium mixture of diastereoisomers *A* and *B* at 0°C, (c) equilibrium mixture of diastereoisomers at −62°C.

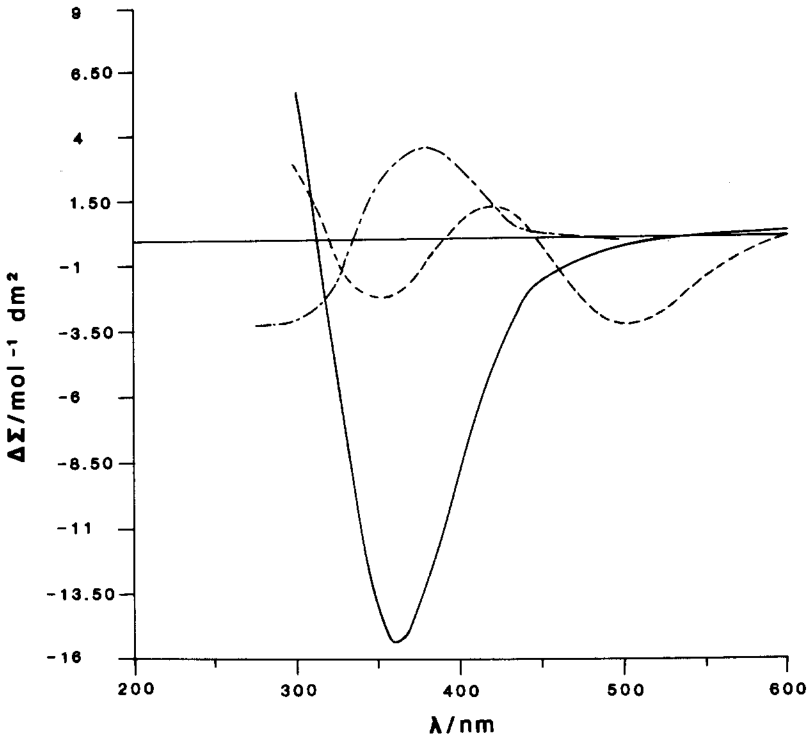

Fig. 2. Circular dichroism spectra of **3** and **4**; ——— (tropone) $Fe(CO)_2L$ (pure diastereoisomer, $CHCl_3$), ------ (tropone) $Fe(CO)_2L$ (equilibrium mixture of diastereoisomers, $CHCl_3$), ·—·—· (isoprene) $Fe(CO)_2L$ (pure diastereoisomer, CH_3CN).

nation to a conjugated cyclic or acyclic triene or tetraene ligand. Samples of **1** of very weak enantiomeric enrichment (ca. 1%) have been prepared by destructive photolysis using circularly polarized light [4], and recently an analytical separation of enantiomers by HPLC has been achieved [5]. Substitution of **1** using (+)-(neomenthyl)PPh_2 [6] yields **3**, whose ^{31}P NMR spectrum reveals an unequal population of two diastereoisomers (vide infra) from which the less abundant isomer may be isolated by fractional crystallisation [6]. Warming to 20°C results in diastereoisomer interconversion via a 1,3-metal shift to yield an equilibrium 1.4/1 mixture (Fig. 1b) [7], which is identical to that obtained from the crude reaction product. Cooling of the equilibrium mixture to $-62°C$ yields a spectrum (Fig. 1c) in which each diastereoisomer exhibits two resonances. By analogy with (tropone)$Fe(CO)_2PPh_3$ [8], these may be assigned to unequal populations of the two geometrical isomers generated on occupation by the phosphine of the two inequivalent basal sites of a square pyramidal geometry. The greatly differing relative populations in the two diastereoisomers may be noted.

In $CDCl_3$, the rate of 1,3-metal shift (6.8×10^{-4} s^{-1} at 33.0°C) [9] is about an order of magnitude faster than that recently reported for the tricarbonyl complex [5]. Comparison of the circular dichroism spectrum of the pure diastereoisomer at 0°C (Fig. 2) with that of the tricarbonyl complex [5] shows that it is derived from the $(-)$-(tropone)Fe$(CO)_3$ isomer, though the absolute configuration is not known. Heating to +30 °C yields eventually the spectrum of the equilibrium mixture (Fig. 2), with the intersections representing isodichroic points.

Though the rate of the 1,3-shift precludes asymmetric syntheses using the pure diastereoisomer at temperatures much higher than +10 °C, we have found that cycloaddition reactions using, for example, tetracyanoethylene [10] are sufficiently rapid at 0 °C and below to provide diastereoisomerically pure adducts. We are also investigatinig the influence of other chiral ligands on the equilibrium diastereoisomeric ratio.

Chiralty in **2** is derived from asymmetric alkyl substitution of the acyclic diene. Substitution using $(+)$-(neomenthyl)PPh_2 yields **4** as an equimolar mixture of two diastereoisomers ($\delta(^{31}P)$ 72.5, 73.6 ppm) from which the isomer of higher chemical shift may be isolated by fractional crystallization [6]. This complex is also fluxional, exhibiting two resonances of approximately equal intensity at −70 °C which may be assigned to axial and basal isomers of a square pyramidal geometry [11]. In contrast to **3** however, there is no evidence for diastereoisomer interconversion at temperatures up to +100 °C. In this case, the absolute configuration has been determined

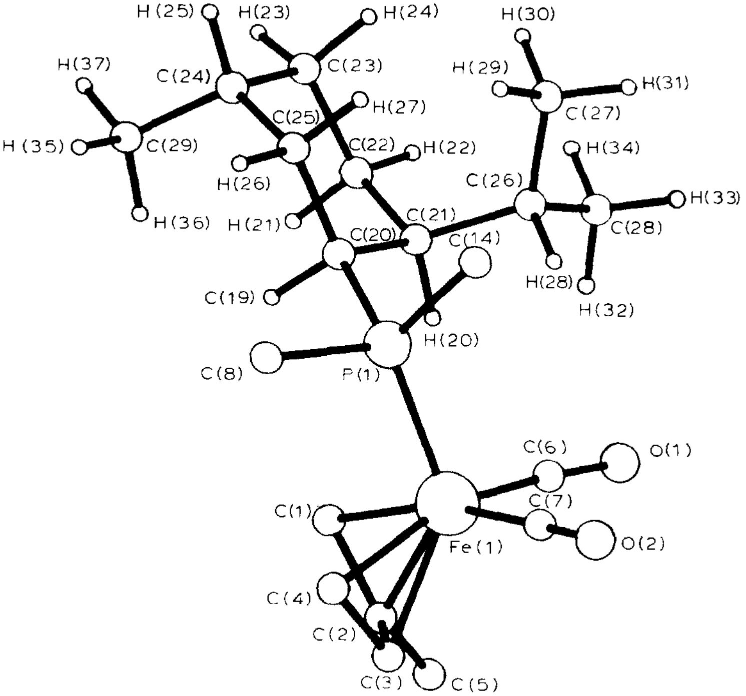

Fig. 3. Structure of complex **4**. Diene hydrogens and C(2)–C(6) of phenyl rings omitted for clarity. Important bond lengths (Å): Fe(1)–P(1) 2.230(3); Fe(1)–C(6),C(7) 1.719(17), 1.777(17); Fe(1)–C(1),C(4) 2.068(16), 2.082(15); Fe(1)–C(2),C(3) 2.063(13), 2.058(15); C(1)–C(2), C(3)–C(4) 1.442(18), 1.492(19); C(2)–C(3) 1.356(17). Important bond angles (°): P(1)–Fe(1)–C(6),C(7) 103.0(4), 99.2(4); P(1)–Fe(1)–C(1),C(4) 91.6(4), 94.9(4); C(1)–Fe(1)–C(4) 79.6(5), C(2)–Fe(1)–C(3) 38.4(5); C(6)–Fe(1)–C(7) 91.5(8).

crystallographically (Fig. 3) *. The overall geometry may be described as a distorted square pyramid with phosphine in the axial position. The known configuration of the neomenthyl group (1*S*, 2*S*, 5*R*) establishes the configuration of the (isoprene)Fe moiety as (2*R*) according to the Birch convention for nomenclature [18].

It has been shown that in reactions which generate chiral quaternary carbon centres (for example, cycloaddition (see above), electrophilic substitution [19], and nucleophilic addition [20]), (diene)- and $[(\text{dienyl})\text{-Fe(CO)}_2\text{PR}_3]^+$ complexes exhibit similar or superior reactivity relative to the tricarbonyl analogue. Thus, pure diastereoisomers of this type should provide access to enantiomerically pure organic products without the need for regeneration of the tricarbonyl enantiomer.

We thank the SERC and the University of Keele for support.

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6 Complexes **3** and **4** were prepared by Me_3NO substitution of **1** and **2** (A.J. Birch and L.F. Kelly, J. Organomet. Chem., 268 (1985) C5) and were fractionally crystallized at 0°C from 8/2 ethyl acetate/petroleum ether (40–60°C) and petroleum ether (40–60°C), respectively. Satisfactory analytical and spectroscopic data were obtained.

7 Based on integrated intensity. Spectral lines are of unequal broadness at 20°C, but a true high temperature limiting spectrum may be obtained in toluene at ca. 60°C.

8 J.A.S. Howell and A.D. Squibb, unpublished work.

9 For A ⇌ B diastereoisomer interconversion, $k_1 + k_{-1} = 6.8\times10^{-4}$ s^{-1}. For $K = 1.4$, $k_{-1} = 4.0\times10^{-4}$ s^{-1} and $k_1 = 2.8\times10^{-4}$ s^{-1}.

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* *Crystal data*: $C_{29}H_{37}O_2PFe$, orthorhombic, space group $P2_12_12_1$, $a = 10.151(2)$, $b = 14.780(2)$, $c = 17.800(3)$ Å, $Z = 4$. $U = 2671.2$. Data were collected on a Hilger and Watts Y290 diffractometer. The unit cell parameters were obtained by a least squares fit of θ values for twelve reflections in the range, $12 < \theta > 20°$. The angles used in the calculation were measured on the diffractometer. The structure was solved by direct methods MULTAN [12] and refined by full matrix least squares using SHELX [13] with 1375 reflections which had $I > 3\sigma(I)$ and 167 variables. Data were corrected for Lorentz and polarization effects but not for absorption. Hydrogen atoms were included in calculated positions. In the final least squares cycle the largest shift/ESD in any parameter was 0.002 and in the difference map the maximum and minimum excursions were equivalent to 0.18 and 0.14 eÅ^{-3}. The residuals were $R = 0.063$ and $R' = 0.068$. The iron and phosphorus atoms and the carbon monoxide groups were refined anisotropically. The thermal parameters were terms U_{ij} of. $\exp(-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + U_{33}l^2c^{\star 2} + 2U_{12}hka^{\star}c^{\star} + 2U_{33}k(b^{\star}c^{\star}))$. The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [14–16]. All calculations were performed on a DEC 2060. The ORTEP program was used to obtain the drawings [17].

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