(Fulvalene)dichromium hexacarbonyl: structure, substitution, and catalytic hydrogenation of conjugated dienes

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$[Fv(Cr_2(CO)_6]$ (Fv = fulvalene, $\eta^5:\eta^5$-$C_{10}H_8$) exhibits the longest hithero known CpCr–CrCp bond and constitutes a catalyst for the radical dihydrogenation of conjugated dienes.

The unique structural constraints and electronic features of the fulvalene ligand have led to the discovery of a number of dincuclear organometallic transformations exhibiting quantitative and qualitative cooperating effects, in comparison to the analogous cyclopentadienyl $(CpM)_2$ complexes.[1,2] In this connection, $[FvCr_2(CO)_6]$ **1**[3] was of particular interest, in light of the expected lability of the Cr–Cr bond. Thus, $[CpCr(CO)_3]_2$ and its derivatives exist in equilibrium with the corresponding 17-electron monomers[4] which readily undergo a variety of typical reactions, in particular, ligand substitution[5] and hydrogenation.[6] With respect to the latter, $[CpCr(CO)_3H]$ and $[CpCr(CO)_3]_2$ function as stoichiometric and catalytic, respectively, dihydrogenation agents of conjugated dienes.[7] Prompted by recent activity in the area,[1c] we report here some of the related chemistry of **1**.

Compound **1** was made in 71% yield, using an improvement to our first procedure,[3a] by treatment of $Na_2{}^+Fv^{2-}$ with $[Cr(CO)_3(MeCN)_3]$ to furnish pale yellow solutions of $\mathbf{1}^{2-}$, which was diprotonated with CF_3CO_2H, and then filtered in air through alumina. Slow crystallization from thf–diethyl ether gave black–green blades of **1** which were subjected to X-ray analysis (Fig. 1).† The molecule is isostructural with the analogous $[FvMo_2(CO)_6]$[8] and $[FvW_2(CO)_6]$,[9] with a fulvalene bend angle of 13° and torsion angle of 4.7°.

Most striking is the intermetallic distance of 3.471 Å, to our knowledge the longest CpCr–CrCp bond measured.[10] It is also greater than the intermetallic separation in the other two members of the triad. In spite of these findings, **1** shows no directly observable sign of thermal metal–metal bond cleavage (^1H NMR, SQUID, EPR),[1c] although its chemistry seemingly features the latter prominently. Thus, at room temperature, fast simple exchange occurs in the presence of ^{13}CO (4 atm, NMR), and exchange coupled with electron transfer takes place with $P(OMe)_3$ (6 equiv., thf, 48 h, 79%), furnishing the red zwitterionic $\{FvCr(CO)_3{}^-Cr(CO)_2[P(OMe)_3]_2{}^+\}$ **2**,‡ a process precedented for $(CpCr)_2$[5a,b,10c] and FvM_2 complexes.[2b,3b,11] Reduction of **1** with Na–Hg or $Li^+BHEt_3{}^-$ (thf) produced solutions of the very sensitive, yellow $\mathbf{1}^{2-}$ which could be protonated (CF_3CO_2H, 0 °C) to the unstable dihydride $[FvCr_2(CO)_6H_2]$ **3**, both characterized spectroscopically (IR, NMR).[1c] Methylation of $\mathbf{1}^{2-}$ (MeI, 2 equiv., thf, −78 °C to 0 °C) resulted in $[FvCr_2(CO)_6Me_2]$ **4** as a yellow, unstable powder.‡ Irradiation of **4** in thf (Rayonet, 300 nm) led, in addition to some decomposition, to the generation of **1** and CH_4, but not of CH_3CH_3 or $CH_2{=}CH_2$.

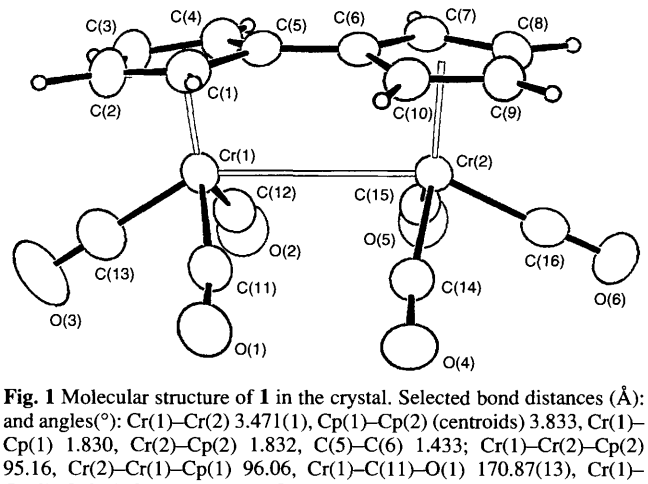
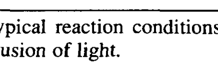
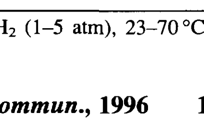


Fig. 1 Molecular structure of **1** in the crystal. Selected bond distances (Å): and angles(°): Cr(1)–Cr(2) 3.471(1), Cp(1)–Cp(2) (centroids) 3.833, Cr(1)–Cp(1) 1.830, Cr(2)–Cp(2) 1.832, C(5)–C(6) 1.433; Cr(1)–Cr(2)–Cp(2) 95.16, Cr(2)–Cr(1)–Cp(1) 96.06, Cr(1)–C(11)–O(1) 170.87(13), Cr(1)–C(12)–O(2) 170.28(14), Cr(1)–C(13)–O(3) 178.64(15), Cr(2)–C(14)–O(4) 171.91(13), Cr(2)–C(15)–O(5) 171.28(13), Cr(2)–C(16)–O(6) 177.80(12), Cp(1)–Cr(1)–C(11) 125.93, Cp(1)–Cr(1)–C(12) 124.60, Cp(1)–Cr(1)–C(13) 116.22.

The dihydride **3** attacked cyclohexa-1,3-diene instantly (even at −20 °C) to give **1** and cyclohexene, suggesting that **1** might function as a catalyst in the dihydrogenation of conjugated dienes.[1c,6,7] Table 1 summarizes the results of testing this notion.

Several comments are in order with respect to the data in Table 1. Thus, (*i*) while reactions could be executed at atmospheric hydrogen pressure at 23 °C, ^1H NMR monitoring and kinetic runs were conducted at up to 5 atm H_2 and 70 °C; (*ii*) reaction mixtures maintained the deep green colour of the catalyst throughout the hydrogenation experiments; (*iii*) the reproducibility of the rates of conversion and product distribution was ascertained by multiple runs; (*iv*) kinetic studies of entry 1 revealed a first order dependence on hydrogen pressure; (*v*) added CO (CO : H_2 = 1 : 1, 7 atm) had no effect on rates but resulted in visibly cleaner solutions; (*vi*) *cis,trans* equilibration of starting materials during hydrogenation was evident in entries 4 and 5 and, in the absence of H_2, was effected rapidly

Table 1 Catalytic hydrogenations affected by **1**[a]

Entry	Substrate	Products (mol %)
1	Cyclohexa-1,3-diene	Cyclohexene (100)
2	2-Methylbuta-1,3-diene	2-Methylbut-2-ene (95), 2-Methylbut-1-ene (3), 3-Methylbut-1-ene (2)
3	Styrene	Ethylbenzene
4	*cis*-Penta-1,3-diene	*trans*-Pent-2-ene
5	*trans*-Penta-1,3-diene	*trans*-Pent-2-ene
6	5-Methylcyclohexa-1,3-diene	Complex mixture
7	2,6,6-Trimethylcyclohepta-1,3-diene	Complex mixture
8		

[a] Typical reaction conditions: 10 mol% **1**, H_2 (1–5 atm), 23–70 °C, thf, exclusion of light.

to give a clean equilibrium mixture of *cis* and *trans*-penta-1,3-diene = 13 : 87, consistent with thermodynamic data;[12] (*vii*) entry 1 in the presence of D_2 at incomplete conversion revealed deuterium incorporation in starting material and extensive scrambling of the label in product [$^nH_2$]cyclohexene (n = 0–6); however, pure cyclohexene was inert to D_2 in the presence of **1**; (*viii*) cyclohexa-1,4-diene was unreactive under standard hydrogenation conditions (NMR); (*ix*) the product distribution in entry 2 is identical to that reported using catalytic $[CpCr(CO)_3]_2$ and appears to be of kinetic origin;[12] (*x*) entry 8 constitutes a diene isomerization in the lycorane series,[13] catalysed by **1** (even in the absence of H_2).

Consideration of all of the observations and comparison with those made in the $(CpCr)_2$ series[4–7] suggests the operation of an identical mechanism involving **3** in which the two metal centres appear to operate largely independently *via* a radical pair pathway.[14]

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Footnotes

† *Crystal data* for **1**, $C_{16}H_8Cr_2O_6$, M = 400.23, triclinic, space group $P\bar{1}$, a = 6.5072(4), b = 9.6913(8), c = 12.4498(10) Å, α = 75.616(7), β = 84.192(6), γ = 75.556(6)°, U = 735.8 (1) Å^3, Z = 2, D_c = 1.81 g cm^{-1}, μ = 14.71 cm^{-1}. 1927 Measured reflections, 1837 unique reflections, 1758 reflections with $I_o \geqslant 3\sigma(I_o)$ used in refinement, R = 0.0221, R_w = 0.0406

The data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073) by the ω–2θ scan method in the range $3 < 2\theta < 45°$. The structure was solved using MULTAN 11/82 after Patterson methods and refined *via* standard least-squares and Fourier techniques. Hydrogens were refined in least squares with isotropic thermal parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/110.

‡ *Physical data* for **2**: mp 181–182 °C decomp; ^1H NMR (300 MHz, CD_3CN) δ 3.81 ('t', J = 5.5 Hz, 18 H), 4.49 (m, 2 H), 4.91 (m, 2 H), 4.95 (m, 2 H), 5.19 (m, 2 H); $^{31}P\{^1H\}$ NMR (CD_3CN) δ 190.58(s); IR (MeCN) $\tilde{\nu}$/cm^{-1} 1976, 1968, 1900, 1797, 1750; FABMS: *m/z* 620 (M$^+$, 2.4), 143 (100). Anal. for C, H, P satisfactory. **4**: decomp. 35 °C; ^1H NMR [300 MHz, $(CD_3)_2CO$] δ 5.35 (dd, J = 2.1, 2.2 Hz, 4 H), 5.09 (dd, J = 2.1, 2.2 Hz, 4 H), 0.61 (s, 6 H); IR (thf) $\tilde{\nu}$/cm^{-1} 2002, 1929; MS *m/z* 430 (M$^+$, 0.58), 57(100); HRMS Calc. (Found) for $C_{18}H_{14}Cr_2O_6$: *m/z* 429.9600 (429.9589).

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