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Note

Synthesis and characterization of deuterium-labelled (fulvene)$M(CO)_3$ complexes (M = Cr, Mo)

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Abstract

The preparation and characterization of a series of deuterium-labelled (fulvene)$M(CO)_3$ (M = Cr, Mo) complexes is reported. (η^5-6-Dimethylaminofulvene-d_2)$Cr(CO)_3$ and (η^5-6-dimethylaminofulvene-d_2)$Mo(CO)_3$ were obtained in high yields by reacting the deuterated fulvene ligands with $(MeCN)_3M(CO)_3$ (M = Cr, Mo). In addition, syntheses of 6,6-diphenylfulvene-d_{10} and 6,6-diphenyl-1,2-benzofulvene-d_{10} as well as the corresponding tricarbonylchromium complexes are described.

Keywords: Deuteration; Fulvenes; Fulvene complexes; Chromium complexes; Molybdenum complexes

1. Introduction

The organometallic chemistry of pentafulvenes has recently gained renewed interest as fulvenes have been found to be highly versatile starting materials for the preparation of catalytically active metallocenes. Various olefin polymerization catalysts have been prepared from fulvenes such as 6,6-dimethylfulvene or 6-dimethylaminofulvene [1–4]. (Fulvene)$Cr(CO)_3$ complexes form a well-established group of transition metal fulvene derivatives. Since their discovery by Fischer et al. more than 40 years ago [5], these compounds have been extensively investigated using spectroscopic as well as X-ray crystallographic techniques [6]. Some uncertainties, however, remained in the unequivocal assignment of the ^{1}H NMR signals of the coordinated fulvene ligands. We report here the preparation and characterization of deuterium-labelled tricarbonyl(fulvene)chromium and molybdenum complexes which allowed an unambiguous ^{1}H NMR analysis of the coordinated fulvenes.

The ^{1}H NMR spectra of (fulvene)$Cr(CO)_3$ complexes containing 6-alkyl- and 6-aryl-substituted fulvenes (**1**, **2**) in all cases display the sequence $\delta_{H2,3} > \delta_{H1,4}$ for the ring protons (AA'XX' system) [6] (Scheme 1).

In the case of the 6-dimethylaminofulvene complexes **3a–c** (Scheme 1), the signals of the ring protons overlap and no definite assignment could be made. A similar problem was encountered in the ^{1}H NMR spectrum of the complex (η^6-6,6-diphenyl-1,2-benzofulvene)$Cr(CO)_3$ (**4**) [7]. The synthesis of tricarbonylchromium complexes of 6-dimethylaminofulvene-d_2 and 6,6-diphenyl-1,2-benzofulvene-d_{10} should allow an unambiguous assignment of these ^{1}H NMR spectra.

2. Experimental

All reactions involving metal carbonyl complexes were carried out under dry nitrogen using standard Schlenk techniques. THF was dried over Na/benzophenone and freshly distilled under nitrogen prior to use.

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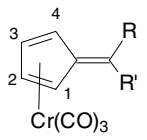
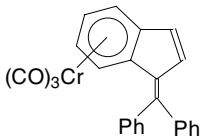


1: R, R' = alkyl
2: R, R' = aryl
3a: R = H, R' = NMe_2
3b: R = SMe, R' = NMe_2
3c: R, R' = NMe_2



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Scheme 1. (Fulvene)$Cr(CO)_3$ complexes.

Commercially available C_6D_6 and dicyclopentadiene were used without further purification. 6-Dimethylaminofulvene-d_2 [8] and $(MeCN)_3M(CO)_3$ (M = Cr, Mo) [9,10] were prepared as described in the literature. Although benzophenone-d_{10} is commercially available, it was synthesized via an improved method following a procedure given by Staudinger [11]. IR spectra: Perkin–Elmer spectrometer 180 and Bio-Rad FTS 7, Nujol mulls between KBr disks. ^{1}H NMR spectra: and Bruker AM-250 (250 MHz, TMS ext., 25 °C).

2.1. (η^5-6-Dimethylaminofulvene-d_2)$Cr(CO)_3$ (**5a**)

A solution of $(MeCN)_3Cr(CO)_3$ (3.73 g, 13.4 mmol) and 6-dimethylaminofulvene-d_2 (1.63 g, 13.4 mmol) in THF (250 ml) was stirred for 3 d at room temperature. The resulting deep red reaction mixture was filtered, 100 ml of *n*-heptane was added to the filtrate, and the solution was concentrated in vacuo to a total volume of 50 ml. The precipitate was isolated by filtration, washed with *n*-pentane (20 ml) and dried under vacuum to give 3.16 g (91%) of glistening, dark red platelets. M.p. 238 °C (dec.). *Anal.* Calc. for $C_{11}H_9CrD_2NO_3$ (259.2): C, 50.97; H, 3.50; D, 1.56; N, 5.40. Found: C, 51.36; H, 3.46; D, 1.54; N, 5.20%. IR (KBr): ν(CO) 1904, 1816, 1784; ν(C=N) 1622 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.85 (s, H-6), 5.08 (s, H-2,3), 3.46 (s, 3H, CH_3), 3.30 (s, 3H, CH_3) ppm. ^{13}C NMR (acetone-d_6): δ 240.4 (CO); 155.4 (C-6); 89.9 (C-1,2,3,4); 80.8 (C-5); 47.9, 41.1 (CH_3) ppm.

2.2. (η^5-6-Dimethylaminofulvene-d_2)$Mo(CO)_3$ (**5b**)

The analogous reaction of $(MeCN)_3Mo(CO)_3$ (1.50 g, 4.9 mmol) and 6-dimethylaminofulvene-d_2 (0.6 g, 5.0 mmol) afforded 1.30 g (88%) **5b** as orange-red microcrystals. M.p. >300 °C (dec.). *Anal.* Calc. for $C_{11}H_9D_2MoNO_3$ (303.2): C, 43.58; H, 2.99; D, 1.33; N, 4.62. Found: C, 45.02; H, 2.79; D, 1.24; N, 4.40%. IR (KBr): ν(CO) 1908, 1818 (sh), 1787; ν(C=N) 1616 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 8.02 (s, H-6); 5.67 (m, H-1,4, ca. 30%); 5.51 (s, H-2,3); 3.42 (s, 3H, CH_3), 3,28 (s, 3H, CH_3) ppm. ^{13}C NMR (acetone-d_6): δ 230.0 (CO); 153.6 (C-6); 93.4 (C-1,2,3,4); 87.7 (C-5); 48.3, 41.4 (CH_3) ppm.

2.3. Benzophenone-d_{10} (improved preparation) [11]

Anhydrous $AlCl_3$ (26 g, 0.20 mol) was added in small increments to a stirred solution of oxalyl chloride (12.7 g, 0.10 mol) and C_6D_6 (25 ml, 0.28 mol) in carbon disulfide (50 ml). After the vigorous evolution of DCl had ceased, the brown reaction mixture was refluxed for 2 h and evaporated to dryness. The residue was redissolved in diethylether (150 ml) and the solution was poured onto 300 g of ice. The organic layer was separated, the aqueous phase was extracted with diethylether (3×150 ml) and the combined extracts were dried over Na_2SO_4. Removal of the solvent and distillation of the residue under vacuum (b.p. 83 °C/ 10^{-3} torr) afforded 15.4 g (80%) of pure benzophenone-d_{10}.

2.4. 6,6-Diphenyl-1,2-benzofulvene-d_{10} (**6**)

A solution of sodium ethoxide was freshly prepared from Na (2.0 g, 0.09 mol) and ethanol (100 ml). Benzophenone-d_{10} (12.0 g, 0.06 mol) and freshly distilled indene (10.0 g, 0.09 mol) were added and the mixture was heated to reflux for 8 h. Cooling to room temperature gave a red-brown precipitate, which was isolated by filtration and washed with ethanol (20 ml). The crude benzofulvene was contaminated with a red by-product. Purification was achieved by repeated (2×) chromatography on silica gel (toluene, column: l = 20 cm, ∅ = 6 cm). Subsequent recrystallization from ethanol yielded 15.3 g (84%) of bright yellow crystals. M.p. 111 °C. *Anal.* Calc. for $C_{22}H_6D_{10}$ (290.5): C, 90.98; H, 2.08; D, 6.94. Found: C, 92.08; H, 2.13; D 7.12%. IR (KBr): 1587, 1464, 1352, 783, 764, 685, 533 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.32 - 6.85 (m, H-1′,2′,3′,4′); 6.73, 6.58 (AB, H-3,4, J = 7 Hz) ppm. ^{13}C NMR ($CDCl_3$): δ 146.6, 144.2, 141.9, 141.2, 138.8, 135.8 (quaternary C); 132.0–126.1 (m, C-D); 131.4, 130.3, 127.0, 124.4, 123.4, 120.7 (C–H) ppm.

2.5. (η^6-6,6-Diphenyl-1,2-benzofulvene-d_{10})$Cr(CO)_3$ (**7**)

3.0 g (10.3 mmol) of **6**, dissolved in THF (30 ml), was added to a suspension of $(MeCN)_3Cr(CO)_3$ (3.05 g, 11.8 mmol) in THF (30 ml), and the mixture was stirred for 48 h at 40 °C. The resulting dark red solution was filtered and evaporated to dryness. The residue was redissolved in a minimum amount of toluene and subjected to chromatography on silica gel (column: l = 20 cm, ∅ = 6 cm). Unreacted **6** was eluted with *n*-hexane. Elution with toluene produced a broad red-purple band. Removal of the solvent in vacuo and recrystallization of the residue from *n*-hexane afforded 1.50 g (34%) **7** in the form of red-purple crystals. M.p. 154 °C. *Anal.* Calc. for $C_{25}H_6CrD_{10}O_3$ (426.5): C, 70.41; H, 1.42; D, 4.73. Found: C, 70.46; H, 1.37; D, 4.56%. IR (KBr): ν(CO) 1948, 1863 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.81

(H-4), 6.57 (H-3, AB, $J = 5.6$ Hz), 5.62 (m, H-1′), 5.30 (m, H-4′), 4.96 (m, H-2′,3′) ppm.

2.6. 6,6-Diphenylfulvene-d_{10} (**8**)

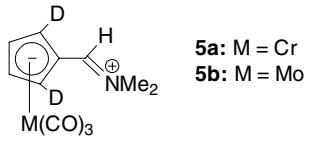
Freshly distilled monomeric cyclopentadiene (6.0 g, 0.09 mol) was added dropwise to a stirred solution of 1.84 g Na and 15.4 g (0.08 mol) benzophenone-d_{10} in dry ethanol (100 ml). After 2 h, the crystalline precipitate was filtered off and recrystallized from ethanol to give 10.8 g (56%) **8** as glistening, bright red crystals. M.p. 79 °C. IR (KBr): 1586, 1463, 1351, 783, 764, 532 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.64–6.56 (m, 2H, fulvene ring-H), 6.33–6.26 (m, 2H, fulvene ring-H) ppm. ^{13}C NMR ($CDCl_3$): δ 151.4 (C-6); 143.5 (C-5); 140.7 (*q*-C_6D_5); 131.9 (C-2,3); 131.3, 127.9, 126.8 (t, *o*,*m*,*p*-C_6D_5); 124.0 (C-1,4) ppm.

2.7. (η^6-6,6-Diphenylfulvene-d_{10})$Cr(CO)_3$ (**9**)

6,6-Diphenylfulvene-d_{10} (**8**) (0.90 g; 3.7 mmol) was added to a solution of $(MeCN)_3Cr(CO)_3$ (0.96 g, 3.7 mmol) in THF (60 ml) and the dark brown reaction mixture was stirred for 24 h at room temperature. The solution was evaporated to dryness in vacuo and the residue was washed with warm *n*-hexane (2×50 ml). The crude product was redissolved in THF (20 ml). Addition of *n*-hexane (20 ml) and cooling to −30 °C yielded 0.40 g (29%) very fine, olive-brown needles of **9**. M.p. 203 °C (dec.). *Anal.* Calc. for $C_{21}H_4CrD_{10}O_3$ (376.4): C, 67.01; H, 1.07; D, 5.36. Found: C, 68.22; H, 0.98; D, 4.91%. IR (KBr): ν(CO) 1969, 1901, 1884 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.38 (t, 2H, fulvene ring-H), 4.63 (t, 2H, fulvene ring-H) ppm. ^{13}C NMR ($CDCl_3$): δ 237.7 (CO), 140.4 (*q*-C_6D_5), 127.9 (m, *o*,*m*,*p*-C_6D_5 + C-6), 107.2 (C-5), 93.2 (C-2,3), 88.6 (C-1,4) ppm.

3. Results and discussion

Treatment of 6-dimethylaminofulvene with a large excess of CH_3OD according to the literature procedure results in ca. 70% deuterium exchange of the 1,4-protons to give 6-dimethylaminofulvene-d_2. This ligand reacted smoothly with $(MeCN)_3M(CO)_3$ (M = Cr, Mo) to afford the desired metal tricarbonyl complexes **5a** and **5b** in high yields.



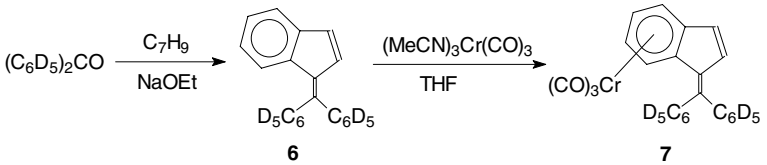
5a: M = Cr
5b: M = Mo

However, the ^1H NMR spectrum of **5a** revealed that in this complex all four ring protons accidentally display the same chemical shift and give rise to only one broad singlet. More helpful was the NMR analysis of the molybdenum analog **5b**. In this case, the ^1H NMR spectrum showed two well-separated signals for the ring protons. The resonance at higher frequency had only ca. 30% intensity and was thus assigned to the 1,4-protons. This is exactly opposite to what is observed in the case of the η^6-coordinated fulvene ligands in **1** and **2** having alkyl or aryl substituents [6]. The sequence $\delta_{H1,4} > \delta_{H2,3}$ was therefore assigned to all $M(CO)_3$ complexes (M = Cr, Mo, W) of 6-dimethylamino-substituted fulvenes [6].

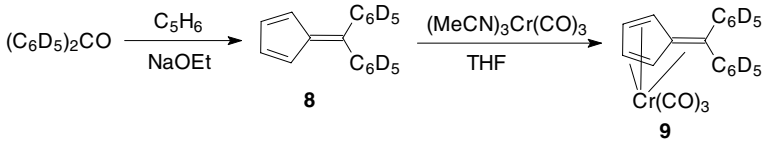
Benzophenone-d_{10} served as starting material for a series of deuterated fulvene and benzofulvenes derivatives. It was found to react cleanly with indene in the presence of sodium ethoxide according to Scheme 2 to give the C_6D_5-substituted 1,2-benzofulvene derivative **6**. The separation of a strongly colored by-product was achieved by repeated chromatography on silica-gel. The tricarbonylchromium complex **7** was synthesized by treatment of **6** with $(MeCN)_3Cr(CO)_3$ in THF [2] (Scheme 2).

The simple ^1H NMR spectrum of **7** clearly confirmed the η^6-coordination of the $Cr(CO)_3$ group. This assignment was not possible in the case of the parent 6,6-diphenyl derivative because of overlap of the fulvene ring resonances with the C_6H_5 multiplets [7]. Starting with benzophenone-d_{10} and monomeric cyclopentadiene, bright red 6,6-diphenylfulvene-d_{10} (**8**) was synthesized in moderate yield (56%). Reaction of **8** with $(MeCN)_3Cr(CO)_3$ in THF afforded olive-brown (η^6-6,6-diphenylfulvene-d_{10})$Cr(CO)_3$ (**9**, Scheme 3). The ^1H NMR spectrum of **9** showed only two triplets corresponding to the ring protons of the fulvene ligand.

The present study shows that various specifically deuterium-labelled fulvene derivatives are readily accessible via different synthetic routes. The highly reactive acetonitrile complexes $(MeCN)_3M(CO)_3$ (M = Cr, Mo) are



Scheme 2. Preparation of 6,6-diphenyl-1,2-benzofulvene-d_{10} and its $Cr(CO)_3$ complex.



Scheme 3. Preparation of 6,6-diphenylfulvene-d_{10} and its $Cr(CO)_3$ complex.

the precursors of choice for synthesizing the corresponding tricarbonylchromium or -molybdenum complexes.

Acknowledgment

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