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ISOLATION OF THE FIRST NEUTRAL CHROMIUM FORMYL DERIVATIVES

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Summary

The first neutral chromium formyl derivative $Cp^{\star}Cr(CO)_2[P(OMe)_3](CHO)$ has been obtained as a *cis-trans* isomers mixture. Both of the isomers, which are remarkably thermally stable, slowly decompose in solution, at different rates, to give *cis*-$Cp^{\star}Cr(CO)_2[P(OMe)_3]H$.

Introduction

The interest in the organometallic chemistry of CO is largely centred on finding new catalytic processes for the conversion of CO into organic chemicals or clarifying the steps of CO reduction in well-known processes (e.g. Fischer–Tropsch). Studies concerned with the latter aspect have led to preparation of formyl derivatives of many transition metals [1]. There is, however, no reported example of an isolated chromium formyl complex; the only studies on this subject have concerned the spectroscopic observation in solution of the unstable anionic $[Cr(CO)_5(CHO)]^-$ [2a,b] and cationic $[Cr(H_2O)_5(CHO)]^{2+}$ [2c] species. Knowledge of the properties of chromium formyl complexes would be of great interest, since a Cr–CHO unit is assumed to be formed in the methanol synthesis carried out in the presence of a ZnO/Cr_2O_3 heterogeneous catalyst [3] and we describe here the synthesis of the first neutral chromium formyl derivative $Cp^{\star}Cr(CO)_2[P(OMe)_3](CHO$ ($Cp^{\star} = \eta^5$-C_5Me_5), which has been isolated as a *cis-trans* isomers mixture.

Results and discussion

The cationic chromium carbonyl $[Cp^{\star}Cr(CO)_3\{P(OMe)_3\}]BF_4$ (**1**) was made by the method used for the molybdenum analogues [4], involving hydride abstraction

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from Cp*Cr(CO)$_3$H [5] by [Ph$_3$C]BF$_4$ followed by addition of one equivalent of P(OMe)$_3$. **1** is a thermally stable, moisture-sensitive product. Its spectroscopic characterization IR (Nujol) ν(CO) 2020m, 1970s, 1940vs and ν(BF) 1050vs cm^{-1}; ^{1}H NMR (CD$_3$OD) δ 1.8 (s, 15H, Cp*), 3.75 (d, ^3J(PH) 12 Hz, 9H, PO*Me*) agree well with those for other 18-e cationic four-legged piano-stool complexes of the Cr triad [4]. **1** reacts in ethanol at −20°C with an equimolar amount of NaBH$_4$ to give Cp*Cr(CO)$_2$[P(OMe)$_3$](CHO) (**2**) as yellow microcrystals (see Scheme 1). Solid **2** is thermally stable, and can be stored under nitrogen at room temperature without noticeable decomposition. The IR spectrum of **2** (Nujol) shows ν(CO) absorptions at 1935s and 1850s, which can be attributed to two terminal CO groups in a neutral complex, and a medium intensity absorption at 1600 cm^{-1} characteristic of a η^1-bonded CHO group. In addition, there are two other peaks in the ν(CH) region, at 2680 w and 2560w cm^{-1}; the observation of weak bands in this region has some precedent for mononuclear formyl complexes [6].

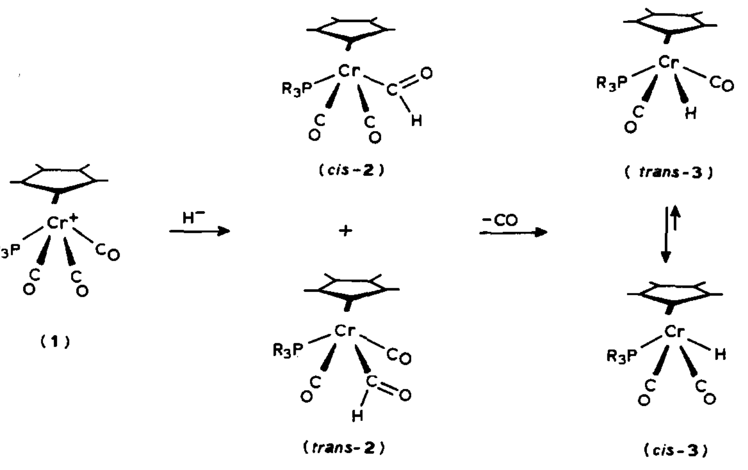
The IR spectrum of **2** in methanol mainly differs from that of the Nujol mull in the shift of the 1600 cm^{-1} band to 1570 cm^{-1}; this effect can be accounted for in terms of hydrogen bonding between the solvent and the formylic oxygen.

The ^{1}H NMR spectrum of **2** exhibited a doubling of all the expected signals thus indicating the presence of *cis-trans* isomers. A double doublet was observed in the formyl region (δ 15.15, ^3J(PH) 6 Hz and 15.00, ^3J(PH) 4 Hz), together with a double doublet for the P(OMe)$_3$ signals (δ 3.70, ^3J(PH) 12 Hz and 3.65, ^3J(PH) 12 Hz) and two singlets for the methyl ring signals (δ 1.83 and 1.80).

The differing decomposition rates of the two isomers, which will be discussed later, allow assignment of the set of signals at lower field to one isomer (δ 15.15, 3.70 and 1.83) and the remaining signals to the other (δ 15.00, 3.65 and 1.80).

All attempts to separate the two isomers were unsuccessful, but a reasonable attribution of their geometry can be made on the basis of literature data for *cis*- and *trans*-(η^5-C$_5$R'$_5$)M(CO)$_2$(L)(R) complexes [7]. In such compounds the *cis*-isomers show lower field ^{1}H NMR signals; moreover, for R = H and L = phosphorous ligand, higher values of J(PH) are reported for the *cis*-isomer. Complex **2** shows similar features, and the isomer exhibiting lower field signals and giving also a larger value of J(PH) (formyl signals) [8] is assumed to be the *cis*-isomer.

When **2** was quickly isolated from the reaction mixture at −20°C the two isomers were approximately in 1/1 ratio (as judged from the ^{1}H NMR spectrum). When **2** was isolated after the reaction mixture had been kept for 3 h at room temperature the isomer ratio was approximately 2/1 (the lower field set of signals being more intense); this observation is consistent [9] with the attribution of the *cis*-geometry to the isomer showing the lower field set of signals. The ^{1}H NMR spectra of an 0.3 *M* solution of **2** (*cis*/*trans*: 1/1) in CD$_3$OD scanned at various times showed complete disappearance of *trans*-**2** after 24 h, whereas about 70% of *cis*-**2** was still present; complete disappearance of *cis*-**2** occurred in 7 d [10]. New signals at δ 3.5 (d, J(PH) 12 Hz) and 1.8 (s, overlapping to the *trans*-**2** Cp* singlet) were observed to grow, while the formyl signals disappeared. No generation of hydride signals could be observed because of fast exchange with the solvent, but with CH$_3$OH as solvent, the appearance of a high field doublet was observed (δ −7.65, ^2J(PH) 100 Hz). The final spectrum is attributed to Cp*Cr(CO)$_2$[P(OMe)$_3$]H (**3**), present as a single isomer; the very large J(PH) observed for the hydride signal is diagnostic for the *cis*-isomer [7]. The formation of the *trans*-**3** isomer cannot be



SCHEME 1

excluded, since it is known that a fast equilibrium, often completely shifted towards the *cis*-isomer, exists between *cis*- and *trans*-$CpM(CO)_2(PR_3)H$ [7]. When the decomposition reaction was complete *cis*-**3** was isolated and characterized. The thermal decomposition of formyl complexes **2** occurs entirely via decarbonylation, the phosphite ligand never being lost ($Cp^{\star}Cr(CO)_3H$ was never found among the thermal decomposition products [11]).

This was surprising, since the related formyl complex *trans*-$CpMo(CO)_2(PPh_3)$-CHO (**4**) [12], quickly decomposes at −41°C to give quantitatively $CpMo(CO)_3H$ and free PPh_3; however, the stronger M–P bond formed to $P(OMe)_3$ rather than PPh_3 accounts for both the surprisingly greater thermal stability of **2** compared to that of **4** and the formation of different decomposition products from these complexes.

Experimental

All preparations were carried out by standard Schlenck techniques under purified nitrogen. Solvents were refluxed over a suitable drying agent and distilled under nitrogen prior to use. IR spectra were recorded on a Perkin–Elmer 283B spectrometer and ^1H NMR spectra on a Varian EM 360 spectrometer.

$Cr(CO)_3(CH_3CN)_3$ [13], $Cp^{\star}H$ [14] and $[Ph_3C]BF_4$ [15] were prepared as previously described.

$Cp^{\star}Cr(CO)_3H$

8.62 g (33.3 mmol) of $Cr(CO)_3(CH_3CN)_3$ and an equimolar amount of $Cp^{\star}H$ were mixed under nitrogen in 100 ml of anhydrous methanol. The suspension was stirred for 48 h at room temperature and the solvent then evaporated under vacuum. The yellow residue was extracted with 150 ml of n-hexane, and the extract was filtered then concentrated to 20 ml and kept at −78°C. The yellow microcrystalline solid which separated was filtered off and vacuum dried (5.70 g, 63% yield).

Satisfactory C and H analytical determinations could not be obtained because of the extreme air sensitivity of the product. IR ν(CO) (Nujol) 2000 and 1920 cm^{-1}. ^{1}H NMR (C_6D_6) 1.55 (s, 15H, Cp*), −5.8 (s, 1H, Cr-H). The IR and ^{1}H NMR data compare well with those reported [5].

*[Cp*Cr(CO)$_3${P(OMe)$_3$}]BF$_4$ (1)*

To 1.512 g (5.56 mmol) of Cp*Cr(CO)$_3$H, dissolved in 20 ml of CH_2Cl_2, 1.797 g (5.44 mmol) of [Ph_3C]BF_4 were slowly added in small portions with the vessel cooled to −30°C. A solution of 6.2 mmol of P(OMe)$_3$ in 15 ml of CH_2Cl_2 was added dropwise to the resulting deep green solution and the mixture then slowly warmed to room temperature. The brown solution obtained was treated with 50 ml of Et_2O then cooled to −78°C to give a yellow microcrystalline precipitate. The moisture-sensitive solid was filtered and vacuum dried (1.368 g, 54.6% yield based on Cp*Cr(CO)$_3$H). Found: C, 40.0; H, 5.1. $C_{16}H_{24}BCrF_4O_6P$ calc: C, 39.8; H, 5.0%), ν(CO) (Nujol) 2020m, 1979s, 1940vs cm^{-1}. ^{1}H NMR (CD_3OD) δ 1.8 (s, 15H, Cp*), 3.75 (d, ^3J(PH) 12 Hz, 9H, P(OMe)).

*Cp*Cr(CO)$_2$[P(OMe)$_3$](CHO) (2)*

A solution of 110 mg (2.84 mmol) of $NaBH_4$ in 10 ml of ethanol was added dropwise to a green solution of **1** in 20 ml of ethanol at −20°C. The solution, which quickly become brown, was stirred for a further 10 min, then kept overnight at −78°C. The yellow microcrystalline precipitate was filtered off and vacuum dried, to give 600 mg of product (68%). (Found: C, 48.2; H, 6.4; $C_{16}H_{25}CrO_6P$ calc: C, 48.5; H, 6.35). IR (Nujol) ν(CO) 2680w, 2560w, 1935s, 1850s and 1600m cm^{-1}. ^{1}H NMR (CD_3OD) δ 15.15 (d, ^3J(PH) 6 Hz, 1H, *cis*-**2** C*H*O), 15.00 (d, ^3J(PH) 4 Hz, 1H, *trans*-**2** C*H*O), 3.70 (d, ^3J(PH) 12 Hz, 9H, *cis*-**2** POMe), 3.65 (d, ^3J(PH) 12 Hz, 9H, *trans*-**2** POMe), 1.83 (s, 15H, *cis*-**2** Cp*), 1.80 (s, 15H, *trans*-**2** Cp*).

*cis-Cp*Cr(CO)$_2$[P(OMe)$_3$]H (3)*

0.150 g (0.378 mmol) of a *cis-trans*-**2** mixture were dissolved in CH_3OH (1 ml) and the ^{1}H NMR spectrum was immediately scanned (showing that there was an ca. 1/1 ratio of *cis-trans* isomers); spectra were scanned at intervals until the formyl signals had completely disappeared. The solvent was pumped off to leave a yellow powder, which was washed with cold n-hexane (2 ml) and vacuum dried (120 mg, 86%) (Found: C, 49.30; H, 7.10. $C_{15}H_{25}CrO_5P$ calc: C, 48.90; H, 6.85%). IR (Nujol) ν(CO) 1930vs and 1860s cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$) δ 3.25 (d, ^3J(PH) 12 Hz, 9H, POMe), 1.65 (s, 15H, Cp*), −7.55 (d, ^2J(PH), 100 Hz, 1H, Cr-H).

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8 Though *cis*- and *trans*-**2** show a much smaller J(PH) value, owing to the presence of the CO group in addition to the metal between hydrogen and phosphorus, a difference is still observable (6 vs. 4 Hz).

9 It has been generally observed for ν(CO) in CpM$(CO)_2$ (L)(R) complexes that the *cis*-isomers have higher wavenumber absorption more intense than the lower wavenumber one, and the reverse is true for the *trans*-isomers [7]. No trace of the thermal decomposition product *cis*-**3**, which could have affected the intensity ratio of the IR peaks, was observed in the NMR spectra of these samples.

10 The evidence suggests that: (i) the 1/1 mixture of isomers initially observed is a kinetic rather than thermodynamic mixture; (ii) there is an enhanced reactivity of the CO group *trans* to $P(OMe)_3$.

11 Loss of $P(OMe)_3$, formation of $Cp^{\star}Cr(CO)_3H$ and subsequent substitution of a CO molecule by $P(OMe)_3$, yielding *cis*-**3**, can be excluded since we observed, in separate experiments, that this reaction is very slow in the reaction conditions.

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