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Preliminary communication

Synthesis, characterization, and reactivity of the neutral metal formyl $(\eta^5\text{-}C_5Me_5)(CO)_2(PPh_3)MoCHO$. A new route to monocationic secondary alkoxycarbene complexes $[(\eta^5\text{-}C_5Me_5)(CO)_2(PPh_3)Mo(CHOE)]^+ X^-$ (E = H, Me)

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Abstract

$(\eta^5\text{-}C_5Me_5)(CO)_2(PPh_3)MoCHO$ (**2**) one of the few isolated neutral metal formyls, reacts with the electrophilic reagents CF_3COOH and CH_3SO_3F without disproportionation to give the secondary carbene complexes $[(\eta^5\text{-}C_5Me_5)(CO)_2(PPh_3)Mo(CHOE)]^+ X^-$ (E = H, X = CF_3COO (**4**); E = Me, X = PF_6 (**5**)).

Reactions involving nucleophilic hydride addition to metal carbonyl complexes have been the subject of intense interest in connection with the synthesis of intermediates in CO conversion. However, efforts to synthesise neutral formyl complexes have produced few instances of isolated and fully characterized compounds. Previously, the only neutral metal formyls isolated were $(\eta^5\text{-}C_5R_5)Re(NO)(L)CHO$ (R = H, Me, L = CO [1], R = H, L = PPh_3 [2]) and $(\eta^5\text{-}C_5H_5)(CO_2)(PPh_3)MoCHO$ [3] and the reactions were limited by an electrophile-catalysed disproportionation [2a]. In order to inhibit this indesirable reaction we have used the bulky (C_5Me_5) ligand, the steric and electronic properties of which are well known [4]. We now describe the synthesis and full characterization of the new molybdenum formyl $(\eta\text{-}C_5Me_5)(CO)_2(PPh_3)MoCHO$ (**2**).

The reduction of the carbonyl-containing cationic species $[(\eta^5\text{-}C_5Me_5)(CO)_3Mo(PPh_3)][PF_6]$ (**1**), [5] with $NaBH_4$ in methanol at −50 °C gave the slightly air-sensitive yellow neutral formyl complex $(\eta^5\text{-}C_5Me_5)Mo(CO_2)(PPh_3)CHO$ (**2**) in 90% isolated yield (eq. 1).

Compound **2** was isolated as a 90/10 mixture of the isomers **2**-*trans* and **2**-*cis*,

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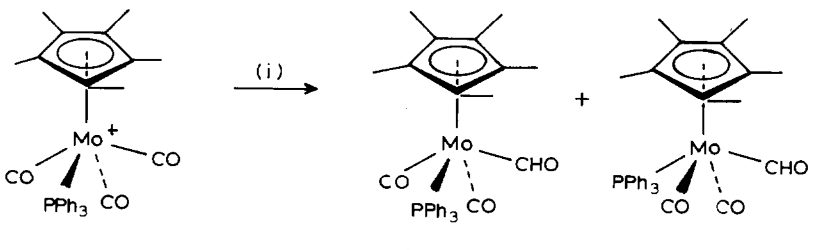
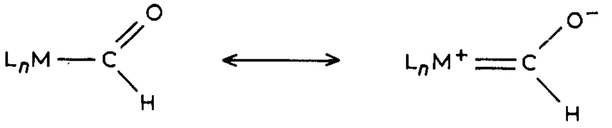


2-*cis* (**1**) **3**-*trans* (**9**) (1)

(i) NaBH$_4$, CH$_3$OH, -50°C

which melts under N$_2$ at 85 °C without decomposition *. The IR spectrum (Nujol mull) has ν(CO) bands at 1932, 1862, 1602 cm^{-1}, and the low stretching frequency for the formyl carbon oxygen bond indicates an important resonance contribution of the zwitterionic form [2] (eq. 2).



$$L_nM{-}C(=O)H \longleftrightarrow L_nM^+{=}C(O^-)H \qquad (2)$$

The 300 MHz ^{1}H NMR spectrum in CD$_2$Cl$_2$ exhibits two characteristic low-field doublets (CHDCl$_2$ as internal standard, with δ 5.30) at 14.28 and 14.60. The *trans* structure is established the main isomer without any ambiguity by the magnetical equivalence of the two CO ligands at 250.4 in the ^{13}C NMR spectrum. In solution no interconversion between the *cis* and *trans* isomers is observed [6 **], but at temperatures up to -20 °C the *trans* isomer decompose slowly to give the known hydride (η^5-C$_5$Me$_5$)(CO)$_3$MoH (**3**) [7] with specific loss of the phosphine ligand. The *cis* isomer of **2** is stable up to 50 °C and its decomposition to give **3** occurs between 60–80 °C during 1 h. In the mass spectrum (170 °C, 70 eV) the metastable molecular ion ($M^+ = 580$) which evolves by loosing CO as shown in the MIKE spectrum [$(M - \text{CO})^+$ found: 552.1120, calc: 552.1152].

In the *trans* isomer ^3J(PH) increases with temperature (-80 °C: 7.5 Hz; -50 °C: 9.3 Hz; -20 °C: 11.9; 0 °C: 13.3 Hz), showing clearly that the relative proportions of rotamers about the M–CHO bond depend on the temperature [8] and suggesting that rotation about this bond is slightly restricted. Use of the ^{1}H NMR NOE effect reveals a 12% enhancement of the formyl proton signal by irradiation of the methyl group of the cyclic ligand in the *trans* isomer, showing that these two ligands are close together, a feature which could inhibit the bimolecular disproportionation during the electrophilic addition.

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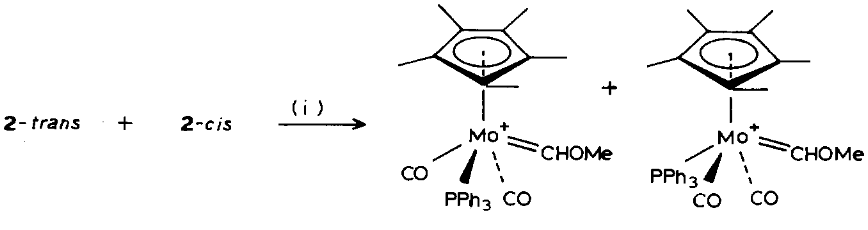
* Data for **2**: IR (Nujol mull, cm^{-1}) 1932, 1862, 1602. ^{1}H NMR (CD$_2$Cl$_2$, -80 °C) 1.70 (s, 15H, C$_5$Me$_5$); 14.28 (d, 0.9H, CHO-*trans*, ^3J(PH) 7.3 Hz); 14.60 (d, 0.1H, CHO-*cis*, ^3J(PH) 5.1 Hz). ^{13}C NMR (C$_6$D$_5$CD$_3$, -50 °C) 10.7 (s, C$_5$Me$_5$; ^1J(CH) 61 Hz); 105.0 (s, *C*$_5$Me$_5$) 250.4 (d, CO, ^2J(PC) 26.0 Hz); 277.8 (dd, CHO, ^2J(PC) 19.7, ^1J(CH) 144.5 Hz). {^{1}H} ^{31}P NMR (C$_6$D$_5$CD$_3$, -50 °C/external H$_3$PO$_4$ 85%) 65.4 (s, 2-*trans*); 71.7 (s, 2-*cis*).

** Reference number with asterisk indicates a note in the list of references.

The reaction of **2** with CF_3COOH (2 equiv.) in CD_2Cl_2 at −70 °C was monitored by ^1H NMR spectroscopy. A single product formed rapidly, and the hydroxymethylene formulation $[(\eta^5\text{-}C_5Me_5)(CO)_2(PPh_3)MoCHOH][CF_3COO]$ (**4**) was assigned to this on the basis of ^1H NMR spectrum, 12.99 (d, 1H, ^3J(PH) 12.6 Hz) for the methylene proton *. There is only one precedent for such a reaction for third row transition metal neutral formyl complexes [2,9 *]. Complex **4** is stable up to +20 °C and attempts are being made to isolate it.

Alkylation of acylmetal carbonyl species provides a well known route to tertiary metal carbonyl carbene complexes [10], but reaction of alkylating agents with neutral formyl metal complexes to give secondary metal carbene has never been reported [2]. However a bicationic metal carbene was recently successfully prepared by *O*-methylation of a cationic formyl complex [11].

The molybdenum formyl complex **2** reacts with CH_3SO_3F at −90 °C in CH_2Cl_2 to give the secondary methoxy carbene $[(\eta^5\text{-}C_5Me_5)(CO)_2(PPh_3)Mo(CHOMe)][PF_6]$ (**5**); work up, followed by metathesis with NH_4PF_6 and recrystalisation of the formed salt from $CHCl_3$ gave **5** as microcristals ** (60% yield).



(3)

(5-*trans*) (5-*cis*)

(i) CH_3SO_3F , CH_2Cl_2 , −80°C

The air-sensitive but thermally stable compound **5** has been characterized by its NMR spectra. The characteristic resonances of the methoxy group appear at 4.02 (**5**-*trans*) and 4.80 (**5**-*cis*) and the carbene protons appear as two broad doublets at 12.52 (**5**-*trans*) and 12.45 (**5**-*cis*) in a ratio which depends on the mode of work-up. ^1H NMR monitoring of this reaction in CD_2Cl_2 at −60 °C reveals the presence of the isomers **5**-*trans* and **5**-*cis* in the same 9/1 ratio as that in the starting formyl complex **2**. Moreover, the intermediate ^1H NMR spectra allow simultaneous observation of **2** and **5**. ^{13}C NMR data clearly confirm the secondary carbene structure, the characteristic downfield doublets for the carbene carbon resonances appearing at 339.33 and 330.5, respectively, for the *trans* and *cis* isomers. The latter

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* Data for **4**: IR (cm^{-1}, CH_2Cl_2) 1930, 1990. ^1H NMR (CD_2Cl_2, 0 °C) 1.74 (s, 15H, C_5Me_5), 12.99 (d, 1H, C*H*OH, ^3J(PH) 146 Hz).

** Data for **5**: IR (cm^{-1}, Nujol) 2030, 1995, 1935, 1130. ^1H NMR (CDC13, 25 °C) **5**-*trans*: 1.95 (s, 15H, C_5Me_5), 4.02 (s, 3H, O-CH_3); 7.60 (m, 15H, PPh_3); 12.45 (d, 1H, C*H*OMe, ^3J(PH) 5.5 Hz). **5**-*cis*: 1.96 (s, 15H, C_5Me_5), 4.80 (s, 3H, O-CH_3); 7.60 (s, 15H, $P(C_6H_5)$); 12.52 (d, 1H, C*H*OMe, ^3J(PH) 1.5 Hz). {^1H} ^{13}C NMR ($CDCl_3$, −50 °C). **5**-*trans*: 10.70 (s, C_5*Me*$_5$); 66.38 (s, CH_3O-); 108.81 (s, *C*$_5Me_5$); 118.49 (d, PPh_3 *ipso*, ^1J(PC) 87.5 Hz); 131.64 (m, PPh_3); 227.57 (d, CO, ^2J(PC) 30.5 Hz) 339.33 (d, *C*HOMe, ^2J(PC) 25.4 Hz). **5**-*cis*: 10.66 (s, C_5*Me*$_5$); 64.94 (s, CH_3O-); 109.37 (s, *C*$_5Me_5$); 118.49 (d, PPh_3 *ipso*, ^1J(PC) 87.5 Hz); 131.64 (m, PPh_3); 233.62 (d,CO, ^2J(PC) 4 Hz); 235.81 (d, CO, ^2J(PC) 29.7 Hz); 330.58 (d, *C*HOMe, ^2J(PC) 6.8 Hz). {^1H} ^{31}P NMR ($CDCl_3$, external H_3PO_4, −50 °C, 85%). **5**-*trans*: 54.62 (s, PPh_3). **5**-*cis*: 52.79 (s, PPh_3); −143.81 (PF_6, J(PF) 713 Hz).

gives two doublets at 233.62 and 235.81 for the CO ligands, while the *trans* compound gives only a single doublet at 227.57. These data are consistent with those previously reported for a related compound in the C_5H_5 series obtained by hydride abstraction [12]. Those examples of addition of an *O*-electrophile to the sterically protected formyl ligand open a new route to secondary heterocarbene complexes with various E fragments; their syntheses and reactivity are at present under investigation in our laboratory.

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