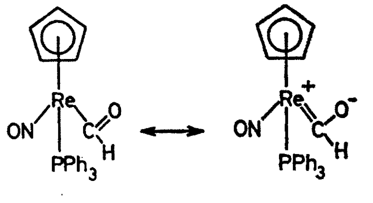
X-Ray Crystal Structure and Chemical Transformations of the Neutral Metal Formyl $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)]$

By Wai-Kwok Wong, Wilson Tam, C. E. Strouse, and J. A. Gladysz*
(*Department of Chemistry, University of California, Los Angeles, California* 90024)

Summary The first X-ray crystallographic analysis of a metal complex containing a formyl ligand (1) and its reactions at room temperature with electrophiles and reducing agents are described.

We recently reported the isolation of the stable (decomp. *ca.* 91 °C; sealed capillary) neutral formyl $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)]$ (1) from the reaction of $LiEt_3BH$ with $[(\eta\text{-}C_5H_5)Re(PPh_3)(NO)CO]^+BF_4^-$ in tetrahydrofuran (THF).[1] Whereas most neutral formyl complexes have been only partially characterized owing to their instability at room temperature,[1–3] (**1**) can be obtained in crystalline, analytically pure form. In the light of the postulated intermediacy of catalyst-bound formyls in some Fischer–Tropsch processes[4] and the lack of structural data on isolable anionic[5,6] or neutral[7] formyl complexes, we have undertaken the *X*-ray crystallographic and chemical characterization of (**1**), the results of which are reported herein.



(1a) **(1b)**

Crystals of (**1**) were grown by the slow diffusion of light petroleum (b.p. 30—50 °C) into a THF solution of (**1**). *X*-Ray data were obtained at -160 ± 5 °C using monochromated Mo-K_α (0·71069 Å) radiation on a Syntex P$\bar{1}$ automatic diffractometer.† The general techniques employed have been described.[8] The unit cell was found to be monoclinic, space group $P2_1/c$ ($Z = 4$), with lattice parameters $a = 8{\cdot}065(3)$, $b = 15{\cdot}156(3)$, $c = 16{\cdot}896(4)$ Å, $\beta = 95{\cdot}44(2)$°. Of 4069 reflections with $2\theta < 50°$ collected, 2914 with $I > 3\sigma(I)$ were used in the final refinement. The final R index was 0·044 with $R_w = 0{\cdot}056$; the atoms Re, C(1), O(1), N, O(2), and P (see Figure) were refined with anisotropic temperature factors and all other non-hydrogen atoms were refined with isotropic thermal parameters. All hydrogens were located from a difference Fourier map. The formyl hydrogen, H(1), was refined isotropically. All other hydrogen atoms were held at positions indicated from the map with assigned isotropic thermal parameters.‡§

The molecular structure of (**1**) is depicted in the Figure. Apart from the expected NO, C_5H_5, and PPh_3 metal–ligand geometries, the most striking structural feature is the short rhenium–formyl carbon bond distance [2·055(10) Å]. The rhenium–acyl bond length in [$(CO)_5Re(p\text{-}COC_6H_4Cl)$] is 2·22 Å,[9] and the average rhenium–(acyl/carbene) bond length in Lukehart's cyclic [$(CO)_4Re[C(Me)O\text{–}H\text{–}OCMe]$] is 2·16 Å.[10] Together with the formyl i.r. stretching frequency {1558 cm^{-1}, as compared to 1624 cm^{-1} in [$(C_5H_5)Re(CO)(NO)(CHO)$]}[1] a substantial contribution to the structure of (**1**) by the resonance form (**1b**) is suggested.

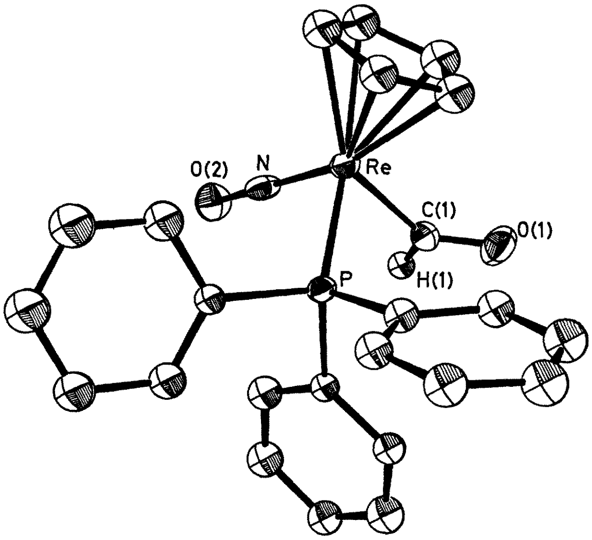


FIGURE. Molecular structure of [$(\eta^5\text{-}C_5H_5)Re(PPh_3)(NO)(CHO)$]. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses are: Re–C(1), 2·055(10), C(1)–O(1), 1·220(12), C(1)–H(1), 1·08(9), Re–P, 2·356(2), Re–N, 1·777(8), N–O(2), 1·190(10), average Re–C(Cp), 2·314(10); ∠Re–C(1)–O(1), 128·1(8), N–Re–C(1), 92·7(4), P–Re–C(1), 85·0(3), P–Re–N, 92·8(3), Re–C(1)–H(1), 119(5), O(2)–N–Re, 178·0(8).

The electron rich nature of the formyl ligand in (**1**) is shown by its chemical reactions. Attempts to obtain formyl oxygen derivatives with an excess of CF_3SO_3H, $MeSO_3F$, or Me_3SiBr at room temperature resulted in the predominant (84—100%) formation of [$(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(CO)$]$^+$ by hydride loss. Anionic formyl complexes act as hydride donors towards a variety of electrophiles,[5,6] but additional observations indicate that these reactions of (**1**) can be considerably more complex and highly dependent upon conditions.[11] Reductive transformation of (**1**) to [$(\eta\text{-}C_5H_5)Re(PPh_3)(NO)(Me)$] [^{1}H n.m.r. $\delta(C_6D_6)$: 6·8—7·8 m, 4·58 s, 1·43 d, $J_{H\text{–}P}$ *ca.* 3 Hz; i.r. (THF): 1630 cm^{-1}] could be accomplished with BH_3·THF (3·7 equiv.; 1·5 h; 72%) or [$(\eta\text{-}C_5H_5)_2ZrClH$] (1·0 equiv.; 16 h;

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† The crystal used was irregularly shaped with approximate dimensions 0·10 × 0·25 × 0·40 mm; it was mounted about the long axis. Data were corrected for a 41% decay in the intensities of three standard reflections. No absorption correction was applied.

‡ All least-squares refinements computed the agreement factors R and R_w according to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2}$, where F_c and Fc are the observed and calculated structure factors, respectively, and $w_i^{1/2} = 1/\sigma(F_o)$. The parameter minimized in all least-squares refinements was $\Sigma w_i||F_o| - |F_c||^2$.

§ Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as supplementary publication no. sup. 22573 (11 pp.) from the British Library. For details of obtaining this material see Notice to Authors No. 7, *J.C.S. Dalton* or *Perkin I* and *II*, Index Issues.

32%). Hence the formyl ligand in (**1**) can be reduced to a methyl ligand, as is postulated to occur[4] on Fischer–Tropsch catalysts.

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