Letter

Deprotonation and Anionic Rearrangements of Organometallic Compounds. III. The First Carbon–Carbon Bond-forming Reaction of an η^1-Formyl Ligand

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Formyl ligands are likely intermediates in the homogeneous, metal-catalyzed conversion of CO/H_2 to oxygenated organic molecules [1 - 7]. As such, their chemistry is of intrinsic interest. Although many metal η^1-formyl complexes have now been isolated [8 - 12], they have not to our knowledge been observed to participate in carbon–carbon bond-forming reactions. In this communication, we describe the first such process, which is initiated by treatment of formyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (1) [13] with strong base.

Reaction of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CHO)$ (1) in THF at −78 °C with $Li^+ {}^-N(i\text{-}C_3H_7)_2$ (LDA, 1.9 equiv, 40 min) and then $CH_3OSO_2CF_3$ (2.6 equiv) gave, after workup, the *formyl*cyclopentadienyl complex $(\eta^5\text{-}C_5H_4CHO)Re(NO)(PPh_3)(CH_3)$ (2) in 68% yield [eqn. (1)]. The structure of 2 followed readily from its ^1H and ^{13}C NMR spectra, which showed patterns characteristic of a monosubstituted cyclopentadienyl ligand [14, 15]. The methyl ^1H NMR resonance exhibited phosphorus coupling (J = 5.8 Hz) typical for a $Re(PPh_3)(CH_3)$ grouping [13], as opposed to a $\eta^5\text{-}C_5H_4CH_3$ ($J <$ 1 Hz) [14, 15] ligand. The migration of the formyl ligand from rhenium to carbon was evidenced by a marked increase in frequency in the IR absorption band corresponding to ν(C=O) (thin film: 1, 1552 cm^{-1}; 2, 1673 cm^{-1}). Summary of the characterization of 2: m.p. 133.5 - 135 °C (dec.). IR (cm^{-1}, thin film): ν(C=O) 1673 (s), ν(N≡O) 1638 (s). ^1H NMR (δ, CD_2Cl_2): 9.27 (s, 1H), 7.47 - 7.33 (m, 15H), 5.57 (m, 1H), 5.01 (m, 2H), 4.56 (m, 1H), 0.79 (d, J_{HP} = 5.7 Hz, 3H). ^{13}C NMR (ppm, CD_2Cl_2): CHO at 185.4 (s), PC_6H_5 at 135.6 (d, J_{CP} = 52.9 Hz, *ipso*), 134.3 (d, J_{CP} = 10.2 Hz), 131.1 (s, *para*), 129.2 (d, J_{CP} = 10.2 Hz); C_5H_4X at 100.7 (s), 95.7 (d, J_{CP} = 4.6 Hz, *ipso*), 92.4 (s), 90.3 (s), 87.6 (s); CH_3 at −30.5 (d, J_{CP} = 7.2 Hz). ^{31}P NMR (ppm, CD_2Cl_2): 19.7 ppm. Mass spectrum (m/e, ^{187}Re, 70 eV); 587 (M^+, 100%), 572 ($M^+ - CH_3$, 26.2%), 262 (PPh_3^+, 71.5%). Analysis: calculated for $C_{25}H_{23}NO_2PRe$; C, 51.19; H, 3.92%. Found: C, 51.19; H, 3.96%.

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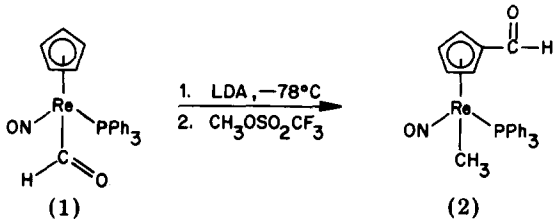
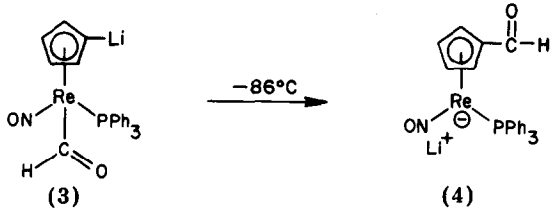


(1) (2) (1)

The reaction of 1 with LDA was monitored by ^{31}P NMR spectroscopy at −86 °C. The starting material (16.0 ppm) was rapidly converted to a new species with a resonance at 32.3 ppm (br m). After 5 min, a new resonance at 41.6 ppm (br m) was also observed. This replaced the 32.3 ppm resonance over the course of 50 min. Subsequent addition of $CH_3OSO_2CF_3$ (−86 °C) gave 2 (20.1 ppm) and other lesser products (25.3, 25.1, 24.7, 23.2 ppm) which, with time and/or warming, decreased as 2 increased. In a separate experiment, (η^5-C_5H_5)Re(NO)(PPh_3)(CDO) (1-d_1; (95 ± 2):(5 ± 2) d_1/d_0) was treated with LDA and then $CH_3OSO_2CF_3$ as described above. The product was shown by mass spectral analysis to be (η^5-C_5H_4CDO)Re(NO)(PPh_3)(CH_3) (2-d_1; (95 ± 2):(5 ± 2) d_1/d_0).

Based upon the above data, and observations with analogous acyl complexes [14], we propose that formyl complex 1 is initially deprotonated on the *cyclopentadienyl* ligand to give (η^5-C_5H_4Li)Re(NO)(PPh_3)(CHO) (3) [eqn. (2)]. We assign the 32.3 ppm ^{31}P NMR resonance to 3, and propose that the formyl ligand undergoes a subsequent migration to give rhenium-centered anion Li^+ [(η^5-C_5H_4CHO)Re(NO)(PPh_3)]$^-$ (4) [eqn. (2)]. Anions [(η^5-C_5H_4X)Re(NO)(PPh_3)]$^-$ characteristically have ^{31}P NMR chemical shifts in the 41 - 47 ppm range [14, 15]. Subsequent addition of $CH_3OSO_2CF_3$ gives principally 2. The by-products observed spectroscopically might arise via methylation of the formyl moiety.



(3) (4) (2)

Finally, a 0.95:1.00 mixture of 1 and (η^5-C_5D_5)Re(NO)(PPh_3)(CDO) (1-d_6; (85 ± 1):(15 ± 1) d_6/d_5) was reacted with LDA and then $CH_3OSO_2CF_3$ as in eqn. (1). Careful mass spectrometric analysis of the resulting 2-d_x showed a (92 ± 2):(8 ± 2) ratio of 2-d_0/2-d_1 and a (85 ± 1):(15 ± 1) ratio of 2-d_5/2-d_4. Hence, the rearrangement 3 → 4 is largely intramolecular.

Other researchers have isolated complexes which might plausibly be viewed as arising from carbon–carbon coupling of formyl ligands [16, 17]. For example, Marks has found that when labile η^2-formyl complexes (η^5-$C_5Me_5)_2$(RO)Th=C(H)O are generated from (η^5-$C_5Me_5)_2$(RO)Th(H) and CO, enediolate complexes (η^5-$C_5Me_5)_2$(RO)ThOC(H)=C(H)OTh(OR)(η^5-$C_5Me_5)_2$ are obtained [16 - 18]. However, mechanistic experiments indicate reduction

of the η^2-formyl ligand by its hydride precursor to be the initial step. Similar enediolate complexes can be isolated from the reaction of $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2$ and $[(\eta^5\text{-}C_5Me_5)_2Sn(H)]_2$ with CO [19, 20], but the nature of the carbon–carbon bond-forming steps are as yet unknown.

The carbon–carbon bond-forming rearrangement $3 \rightarrow 4$ suggests new strategies for the trapping of transient formyl complexes. These have potential application in the design of new CO reduction catalysts. Similar anionic rearrangements have recently been observed with a variety of related cyclopentadienyl complexes [14, 21, 22]. Additional details of these reactions will be reported in future publications from this laboratory.

Acknowledgements

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