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Preliminary communication

INTERMOLECULAR REDUCTION OF CO BY IRON AND MOLYBDENUM HYDRIDES

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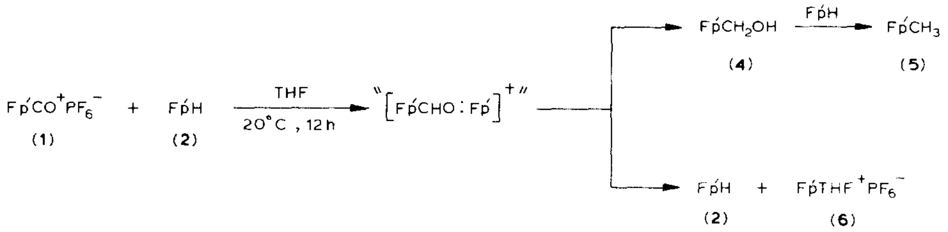
Summary

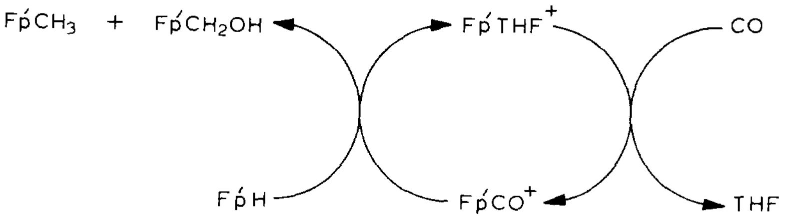
Fp'H (2, Fp' = $C_5(CH_3)_5Fe(CO)_2$) reduces $Fp'(CO)^+PF_6^-$ (1) to $Fp'CH_2OH$ (4) and further to $Fp'CH_3$ (5) and gives $Fp'(THF)^+PF_6^-$ (6) which, under CO recycles the active complex 1; $H_4Mo(dppe)_2$ reduces 1 to Fp'_2 and 4, consistent with the abilities of the Lewis acids to bind the formyl intermediate (BH_3 > $H_3Mo(dppe)_2{}^+$ > Fp'^+).

The well-recognized organometallic mechanisms for homogeneous catalytic CO activation involve CO insertion into metal—alkyl or metal—hydrogen bonds [1]; yet intermolecular reduction of coordinated CO by anionic main group hydrides has been shown to give formyl, hydroxymethyl and methyl complexes with rhenium [2]; and more recently with iron [3,4]. Since clear evidence for true intramolecular insertion of CO into metal—hydrogen bonds in mononuclear complexes under ambient conditions is very rare [5], the feasibility of intermolecular paths for the reduction of CO by transition metal hydrides must be considered [6]. Accordingly we now report the reduction of $[C_5Me_5Fe(CO)_3]^+$-PF_6^- (1) by the neutral transition metal hydrides $C_5Me_5Fe(CO)_2H$ (2) and $H_4Mo(PPh_2CH_2CH_2PPh_2)_2$, (3) [7]. Recently, we found that $NaBH_4$ reduces 1 to $C_5Me_5Fe(CO)_2CH_2OH$ (4), $C_5Me_5Fe(CO)_2CH_3$ (5), or $C_5Me_5Fe(CO)_2H$ (2) depending on the solvent [4]. It is now of interest to compare the reductions by main-group and transition metal hydrides.

1 (1 mmol) reacts with 2 (1 mmol) in THF (10 ml) at 20°C (12 h) to give the hydroxymethyl 4 complex (10% vs. 1) which further gives the methyl complex 5 (10% vs. 1); 2 (70% vs. 1) and $[(C_5Me_5Fe(CO)_2(THF)]PF_6$ (6) (65% isolated vs. 2) [8] (Scheme 1). Given this preliminary result, we set up a system aimed at reducing CO directly using the iron hydride complex 2 as the hydride source. $(Fp'THF)^+$ serves as the source of Fp'^+, the function of which is to transport

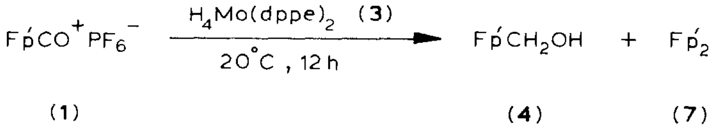


SCHEME 1



SCHEME 2

and activate CO; the cycle is represented in Scheme 2. At 40°C under 1.2 bar of CO and after 2 days, only 150% of CO per mol $(Fp'THF)^+$ is reduced to $Fp'CH_2OH$ and $Fp'CH_3$ using a ratio $Fp'H/Fp'THF = 10$ (30% of Fp'H is consumed). At 20°C under 1.2 bar of CO and after 10 days, 240% of CO per mol $(Fp'THF)^+$ is reduced to $Fp'CH_3$ ($Fp'CH_2OH$, being moderately stable, is now absent) using a ratio $Fp'H/Fp'THF = 100$ (80% of Fp'H is consumed). We believe that these poor turnover numbers are due to the decomposition of the intermediate formyl complex, Fp'CHO, to Fp'H and CO (e.g. the formation of the intermediate formyl complex is probably reversible). The molybdenum hydride complex 3 [7] (1 mmol) reacts with 1 (1 mmol), (12 h, 20°C) giving equal amounts of 4 (15%) and $\{C_5Me_5Fe(CO)_2\}_2$, 7 [9] (15%) (only 30% of 1 is consumed)(eq. 1). This latter product presumably results from electron transfer



$$\underset{(1)}{Fp'CO^+PF_6^-} \xrightarrow[20°C\ ,\ 12\,h]{H_4Mo(dppe)_2\ (3)} \underset{(4)}{Fp'CH_2OH} + \underset{(7)}{Fp'_2} \qquad (1)$$

from 3 to 1, a situation for which precedents exist [10]. It is also worth noting that no product arising from the decomposition of the intermediate formyl complex, $C_5Me_5Fe(CO)_2CHO$, is found, in contrast to the case of the iron hydride 2. Thus, the extent of the reduction of 1 in THF by the B, Mo and Fe hydrides (which proceeds to the methyl complex 5 with $NaBH_4$) is clearly related to the decreasing ability of BH_3, $H_3Mo(dppe)_2{}^+$ and $C_5Me_5Fe(CO)_2{}^+$ (respectively) to behave as Lewis acids toward the coordinated CO and, more specifically, the intermediate formyl complex. The important effect of the strength of the Lewis acid—carbonyl bond has already been revealed by the solvent dependence of the nature of the CO reduction products [2,4].

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