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Preliminary communication

MECHANISM OF THE CARBONYLATION OF DICYCLOPENTADIENYLMOLYBDENUM DIHYDRIDE

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Summary

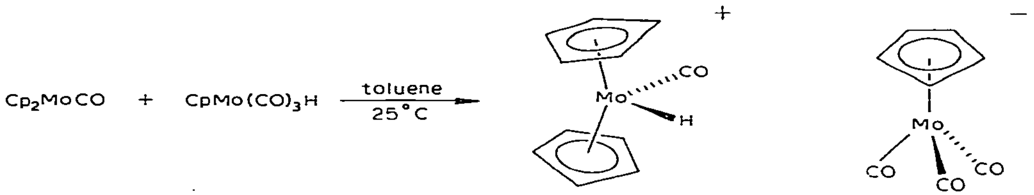
The carbonylation of Cp_2MoH_2 proceeds through the intermediates Cp_2MoCO, $[Cp_2Mo(H)CO]$ $[CpMo(CO)_3]$ (I) and $CpMo(CO)_3H$ to the final products $[CpMo(CO)_3]_2$ and $CpMo(\eta^3\text{-}C_5H_7)(CO)_2$. The formation of I in the carbonylation reaction has been shown to involve net hydride transfer, but an alternate synthesis has demonstrated the considerable proton basicity of Cp_2MoCO. Since the net hydride transfer between Cp_2MoH_2 and $[CpMo(CO)_3]_2$ can be accelerated by production of metal centered radicals, the actual mechanism is not a simple two-electron process (H^- transfer), but rather a sequence of one-electron steps.

We recently reported the reduction (with H_2) of the carbonyl ligand in $Cp_2Ti(CO)_2$ to CH_4 [1]. It was proposed that titanium—oxygen interactions play a crucial role in activating coordinated CO. The same strong affinity of titanium for oxygen which contributes to activation of CO results in production of the very stable cluster $Cp_6Ti_6O_8$; consequently, the reaction is stoichiometric, not catalytic. We are currently examining the CO reduction capability of complexes of other "oxophilic" early transition metals in search of a system where such interactions are kinetically beneficial, yet weak enough to avoid production of catalytically inactive oxo compounds. We have, therefore, examined the carbonylation of Cp_2MoH_2 and related complexes.

The 18-valence electron configuration of Cp_2MoH_2 might be expected to diminish the importance of a simple associative mechanism in the reaction of this dihydride with carbon monoxide. Possible alternative reactions include H_2 elimination, active participation by the cyclopentadienyl rings, and Mo—H bond heterolysis and homolysis. We report here the confirmation of these expectations, including the observation of both intra- and inter-molecular hydrogen transfer reactions.

Treatment of a toluene solution of Cp_2MoH_2 with 1 atm CO at 80°C for 24 h produces a product mixture which contains Cp_2MoCO, $CpMo(\eta^3\text{-}C_5H_7)$-

$(CO)_2$ and an orange solid (I) which is insoluble in toluene.* The identity of the first two products suggests that hydrogen elimination and metal-to-ring migration occur with similar facility under our reaction conditions. Using $(C_5H_5)_2MoD_2$, the deuterium in the resultant $(C_5H_5)Mo(\eta^3\text{-}C_5H_5D_2)(CO)_2$ has been located on the methylene carbons with predominately *cis* stereochemistry (NMR evidence). The insoluble material (I) exhibits infrared absorptions at 2020, 1889, and 1763 cm^{-1} (Nujol), but dissolves in polar solvents to produce spectra which are not only more complex than observed in the solid, but also solvent dependent (see below). This product was characterized as I by a low temperature single crystal X-ray diffraction study and its identity was subsequently confirmed by independent synthesis (eq. 1).

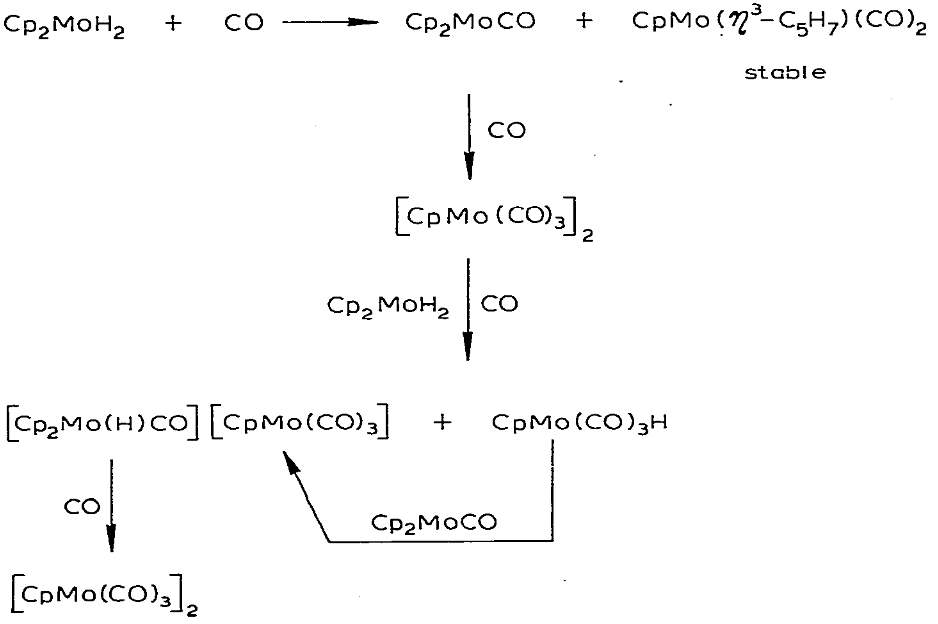


(I)

(1)

On the basis of experiments conducted at higher temperatures and pressures, the overall course of the carbonylation of Cp_2MoH_2 has been established to be that shown in Scheme 1.

SCHEME 1



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*In the product mixture, the intensity of the CO stretching vibration of Cp_2MoCO is approximately twice that of either band of $CpMo(\eta^3\text{-}C_5H_7)(CO)_2$.

The final organometallic products of carbonylation of Cp_2MoH_2 are thus $[CpMo(CO)_3]_2$ and $CpMo(C_5H_7)(CO)_2$. All reactions shown have been verified independently. For example, eq. 2, a formal hydride transfer with heterolysis of the Mo—Mo bond, is complete in 2 h in toluene at 75°C. Since

$$Cp_2MoH_2 + [CpMo(CO)_3]_2 + CO \rightarrow Cp_2Mo(H)CO^+ + CpMo(CO)_3^- + CpMo(CO)_3H \quad (2)$$

eq. 2 is fast compared to the rate of dimer formation, $[CpMo(CO)_3]_2$ is not detected in the carbonylation reaction until all dihydride has been consumed. An analogous heterolysis may also be demonstrated using a main group hydride in THF (eq. 3).

$$2\,BH_4^- + [CpMo(CO)_3]_2 \rightarrow 2\,CpMo(CO)_3^- \quad (3)$$

Further experiments indicate that the thermal hydride transfer in eq. 2 may proceed by two one-electron steps via a radical or radical chain pathway. This has been demonstrated directly in the analogous photoreaction. Irradiation of $[CpMo(CO)_3]_2$ at wavelengths longer that 500 nm causes homolysis to $CpMo(CO)_3$ radicals [2]. Cp_2MoH_2 is essentially transparent above 500 nm; consistent with this, selective irradiation of this dihydride in a stream of CO produces essentially no change. However, irradiation ($\lambda > 500$ nm) of equimolar dimer and dihydride under CO completes the reaction in eq. 2 within minutes at 25°C*. This implicates intermetallic hydrogen atom transfer steps such as eq. 4.

$$Cp_2MoH_2 + CpMo(CO)_3^{\bullet} \rightarrow Cp_2MoH^{\bullet} + CpMo(CO)_3H \quad (4)$$

While the synthesis portrayed in eq. 1 is quantitative in toluene (the salt precipitates), the infrared spectrum of the salt dissolved in THF is characteristic of the coexistence of all four metallic complexes shown in eq. 1. In acetone, this equilibrium shifts wholly towards I. Eq. 1 is stoichiometrically (but not necessarily mechanistically) a proton transfer, and leads to the remarkable conclusion that neutral Cp_2MoCO and anionic $CpMo(CO)_3^-$ have comparable basicity. In hindsight, this is consistent with the estimated [3] pK_a of ~7 for $CpMo(CO)_3H$ and the exceptionally low ionization potential (5.9 ev.) of Cp_2MoCO [4]. For comparison, the infrared spectrum of equimolar $CpMo(CO)_3H$ and Cp_2MoH_2 in THF shows no evidence for proton transfer. The lower basicity of Cp_2MoH_2 correlates with its ionization potential (6.4 eV). However, statistical scrambling of all metal-bound hydride occurs in the time of mixing when $(C_5H_5)_2MoH_2$ is combined with $(C_5H_5)Mo(CO)_3D$ in benzene at 25°C. This result is consistent with (but does not require) a proton transfer equilibrium yielding quantities of $Cp_2MoH_3^+$ and $CpMo(CO)_3^-$ undetectable by infrared techniques.

The variety of hydrogen transfer reactions demonstrated here establishes the versatility of molybdenum hydrides in terms of their ability to react by what is formally either H^+ or H^- transfer. The implication of this work is that

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*The only carbonyl-containing product of photolysis of Cp_2MoH_2 and $Cp_2Mo_2(CO)_4$ in toluene under N_2 purge is Cp_2MoCO.

bimetallic reactions, using one metal complex as a reagent towards a second (not necessarily identical) complex, may serve as a complement to stoichiometric or catalytic intramolecular transformation of a substrate bound to a single metal atom or cluster.

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References

1 J.C. Huffman, J.G. Stone, W.C. Krusell and K.G. Caulton, J. Amer. Chem. Soc., 99 (1977) 5829.
2 N.W. Hoffman and T.L. Brown, Inorg. Chem., 17 (1978) 613.
3 E.O. Fischer, W. Hafner and H.O. Stahl, Z. Anorg. Allgem. Chem., 282 (1955) 47.
4 J.C. Green, S.E. Jackson and B. Higginson, J. Chem. Soc., Dalton Trans. 403 (1975) 403.