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ADDITION OF ACRYLONITRILE TO ANIONIC TRANSITION METAL HYDRIDES. AN IONIC MODEL FOR HOMOGENEOUS OLEFIN PROCESSES

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Summary: The anionic transition metal hydrides, $HM(CO)_4L^-$ (M = Cr, W; L = CO, $P(OMe)_3$) reacted with acrylonitrile and other activated olefins to yield thermally stable addition products, $CH_3CH(X)M(CO)_4L^-$. Kinetic data and electronic substituent effects indicated an associative hydride transfer mechanism.

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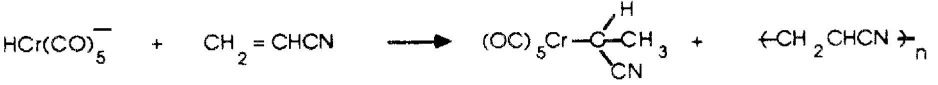
The insertion of olefins into transition metal hydride bonds has been postulated as a key intermediate step in many catalytic processes.[1] The intramolecular insertion process involving both olefin and hydrogen simultaneously bound to the metal can be modelled in the laboratory, particularly for Rh(I) and Nb(III) specie.[2,3] Intermolecular MH/olefin addition via an H• transfer mechanism has been established for $HMn(CO)_5$.[4] Since the highly reactive, isoelectronic $HCr(CO)_5^-$ displays predominantly hydride (H^-) transfer character with polar organic substrates, RC(O)X, RC(O)H, etc.,[5] the characteristics of the reaction of such electron-rich hydrides with olefins were of interest.

Addition of twenty equivalents of acrylonitrile to a THF solution of the anionic hydride $[PPN][HCr(CO)_5]$ resulted in the formation of the thermally stable "inserted" species, $[PPN][CH_3CH(CN)Cr(CO)_5]$, over the course of several hours, eq 1.[6,7] Approximately twelve equivalents of acrylonitrile were required for all of the reactant hydride to be consumed due to the formation of oligomeric acrylonitrile side-products.[8] The structure of the cyanoalkylchromiumpentacarbonyl indicated that the more electrophilic carbon[9] in acrylonitrile accepted the hydride function.



$$HCr(CO)_5^- + CH_2{=}CHCN \longrightarrow \left[(OC)_5Cr{-}C(H)(CN){-}CH_3\right]^- + (CH_2CHCN)_n \qquad (1)$$

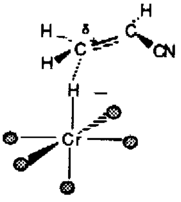
Kinetic studies demonstrated that the reaction (1) obeyed a second order rate equation, rate $= k_2[MH^-][CH_2=CHCN]$, with $k_2 = 4.9\ (\pm\ 0.1) \times 10^{-4}\ M^{-1}s^{-1}$, at 25°C.[10] The velocity of the reaction was unaffected when it was performed under 1 atm of CO, with otherwise identical conditions. Furthermore C-13 labelled CO does not exchange with $PPN^+HCr(CO)_5^-$ in THF at 25°C , either in the absence or in the presence of acrylonitrile, in the time period necessary for the MH^-/olefin reaction to occur. The observed second-order kinetics and activation parameters (obtained from preliminary kinetic data on the $HCr(CO)_5^-/CH_2=CHCN$ reaction: $\Delta H^\ddagger \approx 10$ kcal/mol and $\Delta S^\ddagger$ -38 eu) are consistent with an associative process. Additionally, these activation parameters are quite similar to those for the hydride/halide exchange reaction shown in eq 2, where $\Delta H^\ddagger = +12.6\ (\pm 2)$ kcal/mol and $\Delta S^\ddagger = -30\ (\pm 5$ eu).[11]

$$HCr(CO)_5^- \quad + \quad n\text{-}BuBr \longrightarrow BrCr(CO)_5^- \quad + \quad C_4H_{10} \qquad (2)$$

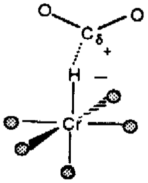
That the most reasonable reaction course for reaction 1 involved a nucleophile/electrophile collision complex was further supported by experiments in which the electronic nature of the olefin was changed. The reactivity of the olefin was found to be dependent upon the electronic effects of the Y substituent on the β-position of the alkene moiety. Under comparable conditions, an order of decreasing reactivity with decreasing electron withdrawal ability of substituent was observed: methyl acrylate > acrylonitrile > acrylamide >> styrene (no reaction) and vinylacetate (no reaction). The lack of reactivity with styrene is a pertinent contrast to the $HMn(CO)_5$/styrene reduction,[4] and argues against a similar H• transfer from $HCr(CO)_5^-$. Preliminary studies have found an enhanced reactivity of activated olefins with more electron rich hydrides: $HCr(CO)_5^- < HW(CO)_5^- < HW(CO)_4P(OMe)_3^-$. This is the same order of reactivity as found in the hydride/halide displacement reactions with organic halides.[5]

An increase in reactivity can also be effected by olefin complexation to a transition metal center.[12] This was observed for the addition of the π-olefin species, $Fe(CO)_4(\pi\text{-}CH_2=CHCN)$[13] to the group 6 transition metal hydrides, $HM(CO)_5^-$. An immediate reaction occurred generating the thermally stable heterobimetallic alkyl complex, $CH_3CH(CN)Fe(CO)_4M(CO)_5^-$, whose spectroscopic parameters[14] are very similar to the thoroughly characterized heterobimetallic alkyl species, $MeFeW(CO)_9^-$.[15] Protonation of this complex with strong acids liberated propionitrile in >90% yields. Thus, metal complexation of the olefin increased its electrophilicity and resulted in the very facile transfer of the hydride to the olefin, in addition to the formation of a stable metal-metal bond.

The above interpretation of our results leads naturally to a representation of the expected collision complex as structure **A**, similar to the proposed acid-base adduct preceding the insertion of CO_2 into the Cr-H of $HCr(CO)_5^-$, **B**.[19] Structure **B** was optimized by **ab initio** LCAO-MO-SCF calculations which indicated the adduct to be more stable than its separated components by 8.4 Kcal/mol.[20]



A



B

Interestingly, although hydrogen is presumably transferred as H$^-$ on both our system and in the *intramolecular* olefin insertion of Cp$^*_2$Nb(η^2-CH$_2$ = CHR)H,[3] substituent effects for the latter are *opposite* those described above. Kinetic parameters for the niobium system argue for Nb-C σ-bond formation early in the transition state and hydrogen transfer as H$^-$ to the substituted β-carbon center later in the transition state. Hence electron releasing groups on the β-carbon stabilize the developing positive charge. In our *intermolecular* process, hydride (H$^-$) transfer to carbon (H-C) precedes M-C bond formation. The reaction is facilitated by electrophilic carbon sites as well as the formation of stable carbanions.

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6. By ν(CO) IR spectroscopy, the reaction was quantitative. Spectroscopic analysis of organometallic product: IR (ν(CO), THF) 2033(w), 1942(w), 1903(s), 1859(m), ν(CN) = 2176 cm^{-1}; ^{1}H NMR (d^6-acetone) 1.16 ppm (q, J = 7.1 Hz), 1.47 ppm (d, J = 7.0 Hz); ^{13}C NMR

227.3, 223.8, 136.1, 25.2, −10.7 ppm. Protonation with stong acids liberates >90% propionitrile. Spectral properties were identical to the product formed from the addition of (±)$CH_3CH(CN)Cl$ to $Cr(CO)_5^{=}$, and also to $[PPN][NCCH_2Cr(CO)_5]$.[7]

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