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**TRANSITION METAL CHEMISTRY UNDER HIGH CARBON MONOXIDE PRESSURE:
AN INFRARED SPECTROSCOPIC STUDY OF CATALYSIS IN THE FISCHER-TROPSCH REACTION**

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- (2) Annual progress report dated January, 1978, covering work performed under Department of Energy Contract EY-76-S-09-0933 during the period January 1, 1977, to December 31, 1977.
- (3) Research proposal entitled "Transition Metal Chemistry under High Carbon Monoxide Pressure: An Infrared Spectroscopic Study of Catalysis in the Fischer-Tropsch Reaction" submitted by R. B. King and A. D. King, Jr., to ERDA in 1975 on the basis of which Contract E(38-1)-933 (now Contract EY-76-S-09-0933) was awarded.
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Metal Carbonyls as Catalysts for the Water Gas Shift Reaction

An important discovery during the previous project period^{2,6} was the observation that simple mononuclear metal carbonyls, specifically $M(CO)_6$ ($M = Cr, Mo, and W$) and $Fe(CO)_5$, were active catalysts for the water gas shift reaction (equation 2). In fact, the high activity of these simple and inexpensive catalyst systems at temperatures around $150^\circ C$ makes such systems of considerable interest for hydrogen production. During the present project period



we have improved the accuracy and convenience of our gas chromatographic analytical technique by the installation of an automated chromatographic data system. We have investigated the catalyst system derived from treatment of $Fe(CO)_5$ with a base (hydroxide, carbonate, or formate) in greatest detail and have observed the following effects of the indicated variables on this reaction:

(1) Solvent: Experiments using various methanol/water solvent mixtures and potassium hydroxide as the base indicate that an approximately 3:1 methanol/water solvent mixture gives the maximum rate of hydrogen production.

(2) Temperature: A series of runs in the temperature range $120^\circ C$ to $160^\circ C$ using the optimum 3:1 methanol/water solvent mixture indicates an activation energy of ca. 29 kcal/mole.

(3) Basicity: If the initial hydroxide concentration is greater than 0.1 M, reaction of hydroxide with CO to give formate occurs in preference to the water gas shift reaction. However, as the hydroxide concentration falls to ca. 0.1 M, this reaction ceases and the water gas shift reaction (equation 2) begins. The latter mode of reaction dominates until all reaction ceases at a pH of approximately 7. The water gas shift reaction is catalytic in base, however, in that the moles of H_2 produced far exceed the moles of base initially introduced into the system. Presumably the CO_2 produced in the $H_2Fe(CO)_4/HFe(CO)_4^-/Fe(CO)_4^{2-}$ system over the pH range in which the water gas shift reaction occurs is $HFe(CO)_4^-$ suggesting that $HFe(CO)_4^-$ is the catalytically active species in these mixtures.

(4) Base Counterion: Using bases containing an alkaline-earth metal counterion ($Ca(OH)_2$ or $Ba(OH)_2$) in 3:1 methanol/water leads to a reaction rate about 10% that of corresponding reactions using a base with an alkali metal counterion (e.g. KOH). Furthermore, the reaction stops completely after a relatively short time with a final pH of approximately 5. This is no doubt a consequence of the insolubility of divalent metal carbonates (i.e. $CaCO_3$ or $BaCO_3$) in the aqueous methanol reaction medium which removes base irreversibly from the reaction solution by the following equation:



Removal of base according to this process results in cessation of the reaction after a short time.

(5) CO pressure: The rate of the reaction is independent of the CO pressure, at least in the pressure range 7 to 30 atmospheres and using potassium hydroxide or sodium carbonate as the base. This suggests that reaction with CO is not involved in the rate-determining step of the reaction mechanism.

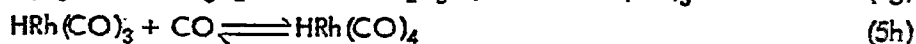
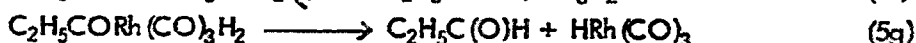
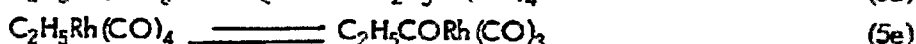
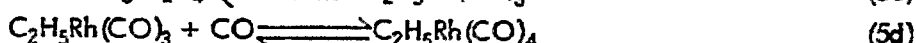
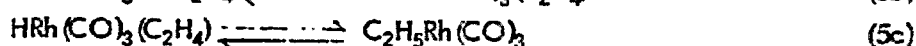
Recently we have begun a similar detailed investigation of the $W(CO)_6$ /base system as a catalyst for the water gas shift reaction (equation 2) in order to assess the effects on the above observation of changing the central metal atom to one having significantly different chemistry. In these studies the role of the solvent system is more pronounced due to the relative insolubility of $W(CO)_6$. Nevertheless, $W(CO)_6$ generates rather active catalyst systems whose detailed features currently are being investigated.

Rhodium Hydroformylation Catalysts

Certain rhodium compounds are known to be active catalysts for the hydroformylation of olefins (e.g. equation 4 in the case of ethylene).^{7,8,9,10} The currently accepted mechanism for such hydroformylation reactions can be summarized by the following



series of equations for the hydroformylation of ethylene with a rhodium catalyst (5a-5h):



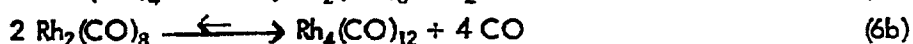
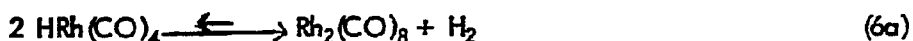
In an attempt to obtain more direct evidence for some of these intermediates we have now investigated reactions of a variety of rhodium complexes with 1:1:1 CO/C₂H₄/H₂ mixtures in our high pressure infrared cell.

Diverse rhodium(I) carbonyl derivatives including $[Rh(CO)_2Cl]_2$, $C_5H_5NRh(CO)_2Cl$, $[CH_3CO_2Rh(CO)_2]_2$, and $C_5H_7O_2Rh(CO)_2$ were found in the high pressure infrared cell to generate systems that catalyse the hydroformylation of ethylene under mild conditions (e.g. 35°C and 20 to 100 atmospheres total pressure). More interestingly, in several such systems, the infrared $\nu(CO)$ frequencies (2115 w, 2037 s, 2019 s cm^{-1}) assigned to an unstable $RRh(CO)_4$ rhodium alkyl were found. The assignments of these frequencies were based on analogy with the reported¹¹ $\nu(CO)$ frequencies of an analogous cobalt compound $CH_3Co(CO)_4$ (2105 w, 2036 m, 2019 vs cm^{-1}). This is the first direct evidence for the existence of rhodium alkyls of the type $RRh(CO)_4$, apparently a very unstable class of compounds. Unfortunately,

Infrared spectroscopy does not provide information on the exact alkyl group attached to rhodium in the $\text{RRh}(\text{CO})_4$ derivative. However, the similarity in the positions of the $\nu(\text{CO})$ frequencies in this $\text{RRh}(\text{CO})_4$ derivative to those listed above for the $\text{CH}_3\text{Co}(\text{CO})_4$ model compound suggests that the electronic properties of the R group in the $\text{RRh}(\text{CO})_4$ derivative must be fairly close to those of the methyl group. It therefore is highly likely that this unknown $\text{RRh}(\text{CO})_4$ derivative is $\text{C}_2\text{H}_5\text{Rh}(\text{CO})_4$, which is involved in steps 5d and 5e of the hydroformylation mechanism. This work is an interesting application of the use of infrared spectroscopy at elevated pressures to detect metal carbonyl intermediates unstable at atmospheric pressure as was suggested in our original research proposal.³

Our studies in the high pressure infrared cell on the hydroformylation of ethylene by various rhodium complexes using a 1:1:1 $\text{CO}/\text{C}_2\text{H}_4/\text{H}_2$ mixture indicated that diverse rhodium(I) complexes are active hydroformylation catalysts under mild conditions but that rhodium complexes containing the metal in other formal oxidation states such as 0 (i.e. $\text{Rh}_4(\text{CO})_{12}$) or +2 (i.e. rhodium(II) acetate) were inactive catalysts under similar conditions. The results with $\text{Rh}_4(\text{CO})_{12}$ were initially somewhat difficult to reconcile with earlier reported observations¹² that $\text{Rh}_4(\text{CO})_{12}$ is an active hydroformylation catalyst for 1-heptene and related liquid substituted olefins. In order to clarify this inconsistency reactions of $\text{Rh}_4(\text{CO})_{12}$ were investigated in n-tetradecane solution using $\text{CO}/\text{C}_2\text{H}_4/\text{H}_2$ mixtures where the ratio of CO to the other gases was varied within a wide range. The results from these experiments are summarized in Table 2. These experiments showed that the maximum rate of hydroformylation was obtained with a $\text{CO}/\text{C}_2\text{H}_4/\text{H}_2$ ratio of 0.2/1.0/1.0. Gas mixtures appreciably richer or poorer in CO led to far slower reaction rates. These data indicate that carbon monoxide, although a necessary reactant for the hydroformylation reaction, is also a catalyst poison possibly by diverting one of the 16-electron intermediates in the catalytic cycle 5a-5h to an inactive 18-electron intermediate by CO addition to the "free" coordination site of the 16-electron intermediate.

Other observations suggest that this CO catalyst poisoning involves diversion of the $\text{HRh}(\text{CO})_3$ intermediate required for step 5b to $\text{HRh}(\text{CO})_4$ (e.g. step 5h). However, $\text{HRh}(\text{CO})_4$ is unstable with respect to $\text{Rh}_4(\text{CO})_{12}$, since both of the equilibria below (6a and 6b) lie predominantly to the right under our reaction conditions in accord with earlier high pressure infrared spectroscopic work by Whyman.¹³ Thus treatment of $\text{Rh}_4(\text{CO})_{12}$ with a 1:1 $\text{C}_2\text{H}_4/\text{H}_2$



mixture in the absence of CO at 35°C and 50 atmospheres results in gradual disappearance of the $\text{Rh}_4(\text{CO})_{12}$ bridging $\nu(\text{CO})$ frequency at 1818 cm^{-1} with the production of a new species exhibiting $\nu(\text{CO})$ frequencies at 2075 and 2026 cm^{-1} . This species (conveniently designated as Compound X) persists in n-tetradecane solution upon release of the $\text{C}_2\text{H}_4/\text{H}_2$ pressure. Solutions containing compound X, as shown by comparison of the $\nu(\text{CO})$ spectra,

TABLE 2

EFFECT OF THE COMPOSITION OF THE CO/C₂H₄/H₂ MIXTURE ON THE HYDRO-FORMYLATION OF ETHYLENE CATALYZED BY Rh₄(CO)₁₂^a

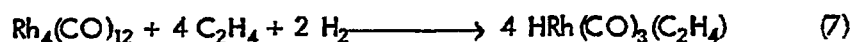
<u>CO/C₂H₄/H₂ Ratios</u>	<u>Production of Propionaldehyde (v(CO) 1/38 cm.⁻¹)</u>
1.0/1.0/1.0	none
0.4/1.0/1.0	none
0.3/1.0/1.0	slow
0.2/1.0/1.0	fast
0.1/1.0/1.0	slow

a) Temperature 37°C, solvent n-tetradecane, partial pressures of C₂H₄ and H₂ each 12 atmospheres.

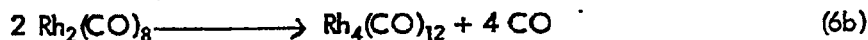
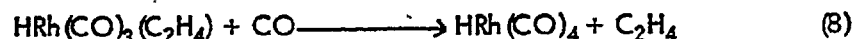
have also been obtained on the preparative scale by reaction of $\text{Rh}_4(\text{CO})_{12}$ with $\text{C}_2\text{H}_4/\text{H}_2$ under pressure at room temperature in an autoclave in pentane solution. A solution of compound X catalyzes the hydroformylation of ethylene using a 1:1:1 $\text{CO}/\text{C}_2\text{H}_4/\text{H}_2$ mixture under conditions where $\text{Rh}_4(\text{CO})_{12}$ is ineffective as a catalyst. Furthermore, treatment of compound X with CO alone results in the regeneration of $\text{Rh}_4(\text{CO})_{12}$.

Our current hypothesis is that compound X is $\text{HRh}(\text{CO})_3(\text{C}_2\text{H}_4)$, a proposed intermediate in the hydroformylation reaction (i.e. steps 5b and 5c). This idea is supported by the following observations:

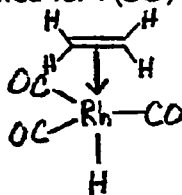
- (1) Its high activity as a hydroformylation catalyst as noted above.
- (2) Its formation from $\text{Rh}_4(\text{CO})_{12}/\text{C}_2\text{H}_4/\text{H}_2$ under mild conditions, possibly by the reaction



- (3) Its reaction with CO to give $\text{Rh}_4(\text{CO})_{12}$ possibly through the following reaction sequence:



- (4) The pattern of its $\nu(\text{CO})$ frequencies is consistent with a trigonal bipyramidal structure I for $\text{HRh}(\text{CO})_3(\text{C}_2\text{H}_4)$ (Calculated for $\nu(\text{CO})$ frequencies: A_1 (weak IR) + E (strong IR)).



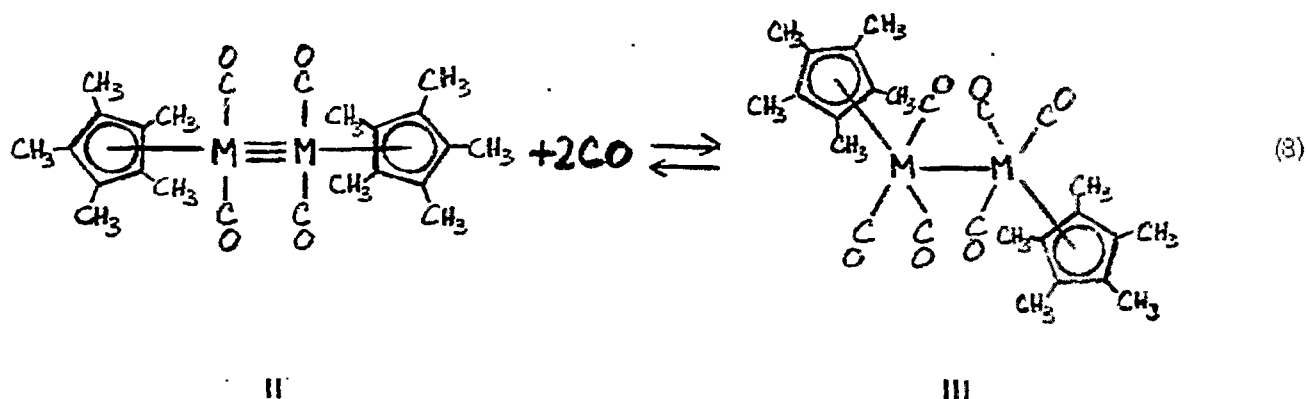
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- (5) The substitution of CO in $\text{HRh}(\text{CO})_4$ with the weaker π -acceptor ethylene should make $\text{HRh}(\text{CO})_3(\text{C}_2\text{H}_4)$ more stable in accord with the ability to detect but not isolate $\text{HRh}(\text{CO})_3(\text{C}_2\text{H}_4)$ as noted above.

This type of evidence for the formulation of Compound X as $\text{HRh}(\text{CO})_3(\text{C}_2\text{H}_4)$ is not particularly convincing. Accordingly, we are in the process of investigating the reactions of the other $\text{M}_4(\text{CO})_{12}$ derivatives ($\text{M} = \text{Co}$ and Ir) with $\text{C}_2\text{H}_4/\text{H}_2$ mixtures hoping to obtain analogous $\text{HM}(\text{CO})_3(\text{C}_2\text{H}_4)$ ($\text{M} = \text{Co}$ and Ir) derivatives which might be stable enough to isolate and therefore to characterize by more convincing chemical and spectroscopic methods.

Additions of Carbon Monoxide to Metal-Metal Triple Bonds

We have now completed our study of the addition of CO to the metal-metal triple bonded derivatives $[(CH_3)_5C_5M(CO)_2]_2$ (II: M = Cr, Mo, and W) to give the corresponding metal-metal single bonded derivatives $[(CH_3)_5C_5M(CO)_3]_2$ (III: M = Cr, Mo, and W) as summarized in the following equation:



Studies of this reaction in the high pressure infrared cell indicate that the ease of CO addition in *n*-tetradecane solution to the metal-metal triple bond in the analogous compounds II (M = Cr, Mo, and W) increases in the sequence Cr < W < Mo. This is the first time that such a comparison between analogous 3d, 4d, and 5d transition metals has been possible. Furthermore, these carbonylations (equation 8) have all been carried out on the preparative scale leading to the isolation of the three metal-metal single bonded $[(CH_3)_5C_5M(CO)_3]_2$, derivatives (M = Cr, Mo, and W) in the solid state. The chromium derivative $[(CH_3)_5C_5Cr(CO)_3]_2$, which was obtained for the first time, is the least stable of these compounds and is red-purple in contrast to the green $[C_5H_5Cr(CO)_3]_2$.

in the communication by Rathke and Feder⁴ reporting that cobalt carbonyl derivatives were active catalysts for the synthesis of methanol, ethanol, and propanol from carbon monoxide and hydrogen. Accordingly, we have begun a systematic study of selected metal carbonyl derivatives as catalysts for the synthesis of alcohols from carbon monoxide and hydrogen using the following two techniques:

(1) Selected metal carbonyl derivatives were heated up to ca. 200°C in n-tetradecane solution under 200 atmospheres of a 1:1 H₂/CO mixture in our high pressure infrared cell.⁵ Infrared spectra were taken periodically in order to determine the metal carbonyl species present at a given temperature. This provides a method for establishing what types of metal carbonyl species are present under conditions resembling those used in the actual catalytic reaction. This is important since it establishes which metal carbonyl precursors lead to different catalytic systems under a given set of reaction conditions.

(2) Catalytic reactions were carried out in an autoclave at 200°C and 200 atmospheres of a 1:1 H₂/CO mixture. Samples were periodically withdrawn over a period of one week and analyzed by gas chromatography. p-Dioxane was used as a solvent in accord with the work of Rathke and Feder.⁴

Our experiments of this type are summarized in Table 1. The highlights of these results up to the present time can be summarized as follows:

(1) Cobalt Derivatives

The cobalt complexes which have been investigated up to the present time fall into two categories: (a) Complexes which form an equilibrium HCo(CO)₄/Co₂(CO)₈ mixture under the reaction conditions as shown by infrared spectroscopy (e.g. CH₃CCO₃(CO)₉ and (C₆H₅)₂C₂Co₂(CO)₈) produce essentially the same mixture of methanol, ethanol, propanol, methyl formate, and ethyl formate as the Co₂(CO)₈ catalyst precursor of Rathke and Feder⁴; (b) Complexes which decompose to carbonyl-free species under the reaction conditions (e.g. [CH₃N(PF₂)₂]₃-Co₂(CO)₂ and (CH₃)₃SnCo(CO)₄) are inactive as catalysts for the hydrogenation of carbon monoxide.

(2) Ruthenium Derivatives

The ruthenium cluster Ru₃(CO)₁₂ forms Ru(CO)₅ as the major product under the reaction conditions as shown by infrared spectroscopy. This ruthenium system is significantly more active than the active cobalt system for the production of methanol from carbon monoxide and hydrogen but is inactive for the production of higher alcohols such as ethanol and isopropanol.

We plan to continue work of this type during the next project period as discussed in detail in our research proposal.

TABLE I. CATALYSTS FOR THE HYDROGENATION OF CARBON MONOXIDE TO ALCOHOLS

Catalyst Precursor	Metal Complexes formed by reaction with 200 atm 1:1 CO/H ₂ ^a		Organic Products formed by the catalyzed reaction of 200 atm CO/H ₂ in dioxane solution ^b		
	Temp.	Products	mmoles/liter	Temp.	Product (mmoles) ^c
Co ₂ (CO) ₈ ^d		HCo(CO) ₄		182°C	MeOH, MeOCO ₂ H, EtOH, EtOCO ₂ H, PrOH
MeCCo ₃ (CO) ₉	200°C	Co ₂ (CO) ₈ ^e	5.5	200°C	MeOH(33.5), MeOCO ₂ H (2.8) EtOH (16.4), EtOCO ₂ H (2.0) PrOH (10.0)
Ph ₂ C ₂ Co ₂ (CO) ₆	180°C	HCo(CO) ₄ /Co ₂ (CO) ₈	5.4	173°C	MeOH, MeOCO ₂ H, EtOH, EtOCO ₂ H, PrOH
(PhP) ₂ Co ₄ (CO) ₁₀	>195°C	HCo(CO) ₄ /Co ₂ (CO) ₈	3.3	~190°C	MeOH, MeOCO ₂ H, EtOH, EtOCO ₂ H, PrOH
[MeN(PF ₂) ₂] ₃ Co ₂ (CO) ₂	160°C	dec. ^f		~200°C	no reaction
Me ₃ SnCo(CO) ₄	>180°C	dec. ^f		~200°C	no reaction
C ₃ F ₇ Co(CO) ₄	~115°C	HCo(CO) ₄ /Co ₂ (CO) ₈ + C ₃ F ₇ CHO(?)	9		
Ru ₃ (CO) ₁₂	>90°C	Ru(CO) ₅	1.5	180°C	MeOH (48), MeOCO ₂ H (4.4)

(a) Unless otherwise indicated these species were identified from their $\nu(\text{CO})$ frequencies in spectra taken in the high pressure infrared cell under the indicated conditions using *n*-tetradecane as the solvent.

(b) These reactions were carried out in an autoclave under the indicated conditions. Liquid samples were removed periodically at 60°C and analyzed by gas chromatography.

(c) The mmoles of the indicated products obtained after 1 week reaction time are given in parentheses.

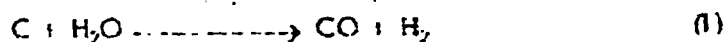
(d) This information was taken from J. W. Rathke and H. M. Feder, *J. Am. Chem. Soc.*, **100**, 3623 (1978).

(e) These products were detected by infrared spectroscopy of the solutions obtained after carrying out the catalytic reactions.

(f) These compounds decomposed under the indicated conditions to give carbonyl-free products as indicated by the absence of $\nu(\text{CO})$ frequencies.

(g) Since this cobalt precursor was shown to give HCo(CO)₄/Co₂(CO)₈ under the reaction conditions, the catalytic reactions were not run.

The ultimate aim of this research project is the discovery of fundamental chemistry which will provide a basis for the substitution of coal for petroleum as a raw material. Since the carbon in coal can be converted to carbon monoxide by the water gas reaction (equation 1), the specific chemistry involved in this project focusses on the basic chemistry behind tech-



nology using carbon monoxide as a raw material. During the period covered by this progress report, various aspects of the fundamental chemistry of the following reactions of carbon monoxide were studied:

(1) The manufacture of alcohols from carbon monoxide and hydrogen: Alcohols can serve as clean fuels for motor vehicles ("gasohol"). Furthermore, if coal-derived carbon monoxide can be substituted for petroleum as a raw material for the manufacture of methanol, ethanol, etc., the scarce petroleum can be conserved for other purposes.

(2) The manufacture of hydrogen from carbon monoxide and water ("water gas shift reaction"): Hydrogen is another candidate for a clean fuel. However, if coal-derived carbon monoxide can be used to liberate the hydrogen from water, then the water gas shift reaction effectively represents a method of getting a clean fuel from coal.

(3) The manufacture of aldehydes from olefins, carbon monoxide, and hydrogen (the hydroformylation reaction): This reaction is important in connection with the manufacture of organic chemicals and uses coal, rather than petroleum, as the source of the aldehyde carbon atom.

Such fundamental chemistry could provide the basis for new and improved molecular catalysts for the above reactions. In the case of both carbon monoxide hydrogenation and the water gas shift reaction, such catalysts might allow industrial processes to be carried out under much milder conditions than those required for the currently used heterogeneous catalysts.

All of the three reactions listed above involve catalysis by transition metal complexes with metal carbonyls as reaction intermediates. Therefore, the high pressure infrared spectroscopic techniques developed during the previous years of this project^{1,2} are very suited to the study of their fundamental chemistry.

The Manufacture of Alcohols from Carbon Monoxide and Hydrogen

The ultimate objective of this research project as envisioned in the original research proposal³ was the development of new transition metal catalysts for the manufacture of hydrocarbon fuels from carbon monoxide and hydrogen (Fischer-Tropsch reaction). Therefore any reaction involving metal carbonyl catalysts which leads to hydrocarbon derivatives is of potential interest to this work. In this connection an interesting report during the past year

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