



Synthesis and Stability Study of a New Bimetallic Complex $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$

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(Received: 31 December 2011;

Accepted: 24 September 2012)

AJC-12169

The present work deals with the preparation and stability study of new bimetallic compound related to hetero bimetallic complex $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$. $\text{Mn}_2(\text{CO})_{10}$ cleaved to $\text{KMn}(\text{CO})_5$ in the presence of Na/K alloy. CuCl and $\text{KMn}(\text{CO})_5$ reacted with triphenyl phosphine in the presence of THF at -78°C . It yielded a mixture of $(\text{Ph}_3\text{P})_3\text{CuCl}$ and $\text{KMn}(\text{CO})_5$. At 0°C , this mixture reacted and produced $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ and Ph_3P . New product $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ was found very sensitive to oxidation. It decomposed into (Ph_3P) , Cu and $\text{Mn}_2(\text{CO})_{10}$ under vacuum, at room temperature.

Key Words: Bimetallic complex, Cu-Mn complex, Heterogeneous catalysis, Infrared Spectroscopy, Stability, Vacuum.

INTRODUCTION

There is considerable interest in hetero bimetallic complexes containing lanthanide and transition metals. They have potential uses as new catalysts¹⁻⁷ or precursors for new materials, such as electro ceramic and chemical sensors⁸⁻¹¹, fluorescent, magnetic properties¹²⁻¹⁶ and rare earth ortho ferrite materials¹⁷⁻²⁰. Metal carbonyls are coordination complexes of transition metals with carbon monoxide²¹. These complexes may be homoleptic, *i.e.* contain only CO ligands, such as nickel carbonyl $[\text{Ni}(\text{CO})_4]$, but more commonly metal carbonyls contain a mixture of ligands, such as $\text{Re}(\text{CO})_5(2,2\text{'-bipyridine})\text{Cl}$. Carbon monoxide is an important building block for the synthesis for many compounds, *e.g.* hydroformylation and metal carbonyl catalysts are central to its utilization. Most metal carbonyl complexes contain a mixture of ligands. Examples include the historically important $\text{IrCl}(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$ and the anti-knock agent $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mn}(\text{CO})_3$. The parent compounds for many of these mixed ligand complexes are the binary carbonyls, *i.e.* species of the formula $[\text{M}(\text{CO})_n]^z$. Formulae of many metal carbonyls are inferred from the 18-electron rule.

Triphenyl phosphine (PPh_3) is a common organo phosphorus compound and widely used in the synthesis of organic and organo metallic compounds. Triphenyl phosphine exists as relatively air stable, colourless crystals at room temperature. The properties that guide its usage are its nucleophilicity and its reducing character. The nucleophilicity of PPh_3 indicated its reactivity toward electrophilic alkenes, such as Michael-

acceptors and alkyl halides. It is also used in the synthesis of bi aryl compounds, such as in the Suzuki reaction²². Triphenyl phosphine binds well to most transition metals, especially those in the middle and late transition metals of groups⁷⁻¹⁰. In terms of steric bulk, PPh_3 has a cone angle of 145° , which is intermediate between those of $\text{P}(\text{C}_6\text{H}_{11})_3$ (170°) and $\text{P}(\text{CH}_3)_3$ (115°). In an early application in homogeneous catalysis, $\text{NiBr}_2(\text{PPh}_3)_2$ was used by Walter Reppe for the synthesis of acrylate esters from alkynes, carbon monoxide and alcohols²³.

In the present work, $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ was synthesized and its stability was studied at 0°C and room temperature respectively.

EXPERIMENTAL

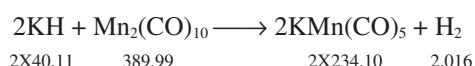
Required chemicals: $\text{Mn}_2(\text{CO})_{10}$ (Merck grade), KH (Merck grade), THF (Merck grade), CuCl (Merck grade), $\text{KMn}(\text{CO})_5$ (Merck grade), Ph_3P (Merck Grade), KCl (Merck grade), pentane (analytical grade), toluene (analytical tgrade), propanol (analytical grade), dry ice (available at Ohio State University, USA), liquid nitrogen.

General procedure: 361.1 mg (0.926 mmol) $\text{Mn}_2(\text{CO})_{10}$ cleaved with 95 mg KH (2.37 m mol) in 10 mL of THF. 96.8 mg CuCl (0.98 mmol) placed in one arm of a two-arm evacuated reaction vessel. 4.9 mL of a 0.19 N $\text{KMn}(\text{CO})_5$ -THF solution (0.94 mmol) was placed in the other arm of flask in a dry box. Cooled to -196°C , evacuated and additional 5.5 mL THF condensed in. After mixing both solutions, the mixture stirred for 60 h at -78°C . The CuCl completely dissolved and a clear

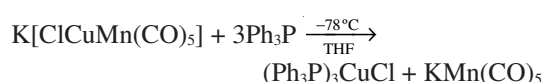
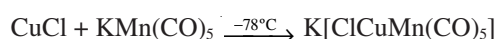
deep green solution was obtained, which probably contained the anion $[(\text{Cl})\text{Mn}(\text{CO})_5]^{-1}$. The anion was very stable thermally and decomposed above $-30\text{ }^\circ\text{C}$ relatively slowly, a stable product was obtained at $-78\text{ }^\circ\text{C}$ under nitrogen and 50 mg of Ph_3P (2.86 mmol). The solution obtained was of brownish red colour. After 2 h stirring, a lot of colourless solid crystallized as $(\text{Ph}_3\text{P})_3\text{CuCl}$ was obtained. The solution stirred over night at $0\text{ }^\circ\text{C}$ and KCl removed through filtration in the dry box. After recrystallization from THF/pentane and toluene/pentane, 430 mg of complex was isolated.

RESULTS AND DISCUSSION

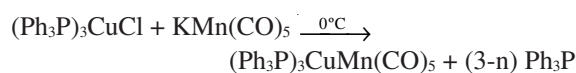
Hetero bimetallic complex $\text{Mn}_2(\text{CO})_{10}$ was cleaved to $\text{KMn}(\text{CO})_5$ in the presence of Na/K alloy.



At $-78\text{ }^\circ\text{C}$ CuCl and $\text{KMn}(\text{CO})_5$ reacted to produce with (Ph_3P) in the presence of THF. It yielded a mixture of $(\text{Ph}_3\text{P})_3\text{CuCl}$ and $\text{KMn}(\text{CO})_5$

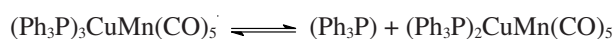


At $0\text{ }^\circ\text{C}$, this mixture reacted and produced $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ and Ph_3P .

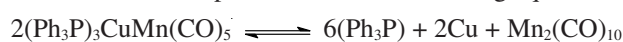


Use of KH: It was found that a yellow precipitate formed contrary to white precipitate. Therefore, experiment was repeated with the KH instead of Na/K alloy. Consequently, white precipitate formed but disappeared and then again, a light yellow precipitate formed.

Cu-Mn bond: Until now, only two complexes of $\text{Mn}(\text{CO})_5$ are available in the literature²¹ which described the single Cu-Mn- δ bond. These two complexes have a copper atom with a three coordinate chelate ligands with arsenic donor atoms. These compounds were reasonably stable toward the air and water. Replacing the three coordinate ligands with three single coordinating Ph_3P ligands altered the stability of $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$. In solution the following equilibrium dominates.



This also expressed that the appearance of the ^{31}P NMR spectrum depends on concentration of free (Ph_3P) in the solution and that the IR spectra of the CO region of $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ and $(\text{Ph}_3\text{P})_2\text{CuMn}(\text{CO})_5$ were practically identical. The other point essentially reduced to the stability of a compound. It was not only very sensitive to oxidation as a solid and in solution, but also decomposed under vacuum in solution at room temperature after the following equation.



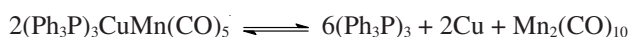
The initiating decisive step is in this case probably was the loss of Ph_3P .

Stability of a bimetallic complex: This consideration was because of the following order of stability specified.



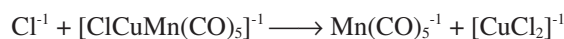
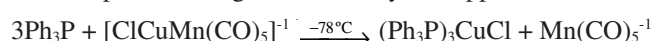
While $(\text{Ph}_3\text{P})_3\text{CuR}$ was well maintained at room temperature, $(\text{Ph}_3\text{P})_2\text{CuMn}(\text{CO})_5$ is already decomposed. These two structures *i.e.* $(\text{Ph}_3\text{P})\text{CuMn}(\text{CO})_5$ and $[\text{ClCuMn}(\text{CO})_5]^{-1}$ exhibited decomposition at about $-30\text{ }^\circ\text{C}$. Special investigations into the reaction mechanism of the formation of $(\text{Ph}_3\text{P})_n\text{Cu-Mn}(\text{CO})_5$ compounds could not be presented.

Stability of $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$: Experimentally it was found that product $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ very sensitive to oxidation. It decomposed into Ph_3P , Cu and $\text{Mn}_2(\text{CO})_{10}$ under vacuum at room temperature.



Findings of reaction schematics: Following observations lead to the formation of the above scheme: (i) In each case a greenish coloured intermediate existed (for $n = 3, 2, 1, 0$), which at least for $n = 0, 1$ was frozen at $-78\text{ }^\circ\text{C}$. (ii) So far as, a reaction of the material in the matrix was prevented then no KCl elimination occurred. (iii) An indication for this was that similar anions do generally existed, for example the isolation of $[\text{Co}(\text{CO})_4]_2\text{Cu}^{-1}$.

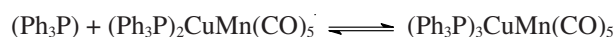
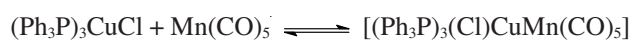
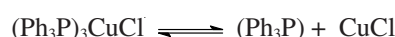
The bond between Cu and Mn in $[\text{ClCuMn}(\text{CO})_5]^{-1}$ was very weak and was easily cleaved with other nucleophiles. So for example following reactions may be happened:



From the observations concerning the general reaction path following conclusions can however be shown:

The formation of a neutral compound appears to occur in every case through a loose adduct, that is an SN_2 mechanism. If $n = 3$, a proposed equivalent analog (i) must be assumed. The equilibration of this equilibrium results very rapidly; for example crystalline $(\text{Ph}_3\text{P})\text{CuCl}$ always appeared in excess Ph_3P , yet not in the presence of free Ph_3P .

That the first step is only necessary for $n = 3$ (similarly the last).



IR analysis: The IR spectrum has been shown in the Figs. 1 and 2, respectively. Three peaks at 1954, 2022 and 2025 cm^{-1} . Two peaks were missing at 1903 and 1880 cm^{-1} .

$(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$: IR ν_{Co} cm^{-1} in THF: 2022 w, sharp, 1952 s, broad, 1909 w, broad.

$(\text{Ph}_3\text{P})_2\text{CuMn}(\text{CO})_5$: IR ν_{Co} cm^{-1} in THF: 2024 w, sharp, 1950 sharp, 1903 m, broad, 1880 sharp.

Single crystal XRD analysis: The single crystal XRD results indicated that crystals of new material were monoclinic and unit cell matched to the $\text{Mn}_2(\text{CO})_{10}$.

Elemental analysis of $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$: The calculated percentage analysis of $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ has been shown in the Table-1.

TABLE-1
ELEMENTAL ANALYSIS (%) OF $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$

	C	H	P	Mn	Cu
Calculated (%)	47.38	2.57	5.96	9.44	10.9

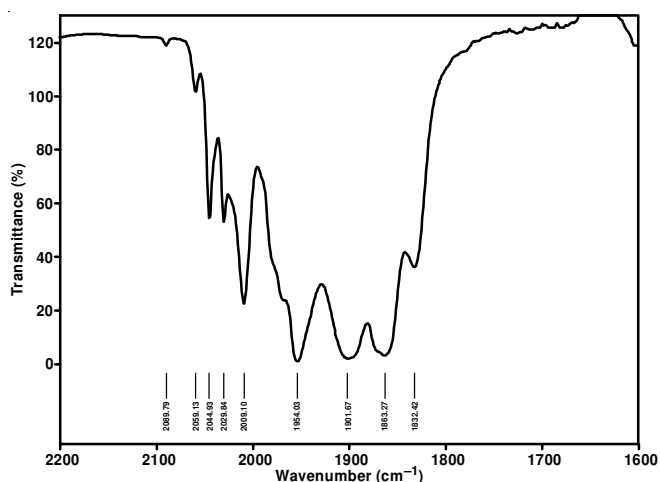


Fig. 1. Infrared spectrum showing presence of $\text{KMn}(\text{CO})_5$

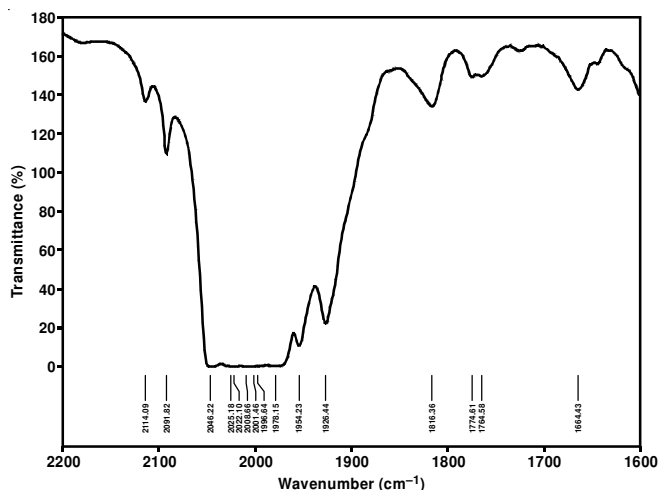


Fig. 2. Infrared spectrum showing presence of $\text{Mn}_2(\text{CO})_{10}$

Conclusion

$\text{Mn}_2(\text{CO})_{10}$ was cleaved to $\text{KMn}(\text{CO})_5$ in the presence of Na/K alloy. At -78°C CuCl and $\text{KMn}(\text{CO})_5$ reacted with (Ph_3P) in the presence of THF. It yielded a mixture of $(\text{Ph}_3\text{P})_3\text{CuCl}$ and $\text{KMn}(\text{CO})_5$. At 0°C , this mixture reacted and produced $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ and Ph_3P . The new product $(\text{Ph}_3\text{P})_3\text{CuMn}(\text{CO})_5$ was found very sensitive to oxidation. It decomposed into $6(\text{Ph}_3\text{P})$, 2Cu and $\text{Mn}_2(\text{CO})_{10}$ under vacuum, at room temperature.

ACKNOWLEDGEMENTS

The authors thank Higher Education Commission (HEC) Government of Pakistan (PIN: IRSIP-4-Ps-15) for providing financial assistance. The authors also thank to Dr. Sheldon G. Shore, Department of Chemistry and Ohio State University, Columbus, Ohio, USA for providing material, guidance and research facilities.

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