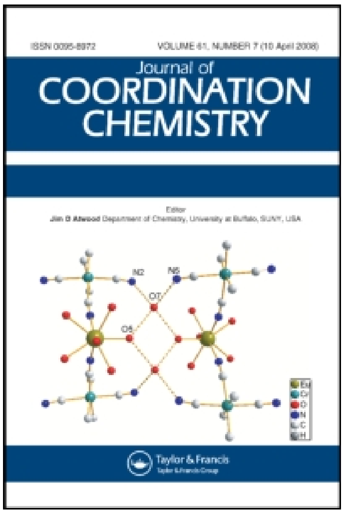

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Zhen, Yueqian and Atwood, Jim D.(1992) 'Single Electron Transfer and CO^{2+} Transfer Reactions of a Disubstituted Cation and Anion, $Mn(CO)_4(PPh_3)^+{}_2$ and $Mn(CO)_3(PPh_3)_2^-$', Journal of Coordination Chemistry, 25: 3, 229 — 232

To link to this Article: DOI: 10.1080/00958979209409195

URL: http://dx.doi.org/10.1080/00958979209409195

J. Coord. Chem. 1992, Vol. 25. pp. 229–232
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SINGLE ELECTRON TRANSFER AND CO^{2+} TRANSFER REACTIONS OF A DISUBSTITUTED CATION AND ANION, $Mn(CO)_4(PPh_3)_2^+$ AND $Mn(CO)_3(PPh_3)_2^-$

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The substitution of triphenylphosphine for CO on cationic and anionic complexes significantly slows single electron transfer reactions (SET) but has a relatively small effect on CO^{2+} transfer. This allows the products of CO^{2+} reactions to be readily identified before subsequent SET reactions can occur. In this manuscript the reactions of the bis-substituted complexes, $Mn(CO)_4(PPh_3)_2^+$ and $Mn(CO)_3(PPh_3)_2^-$, are reported. When the cation is reacted with a metal carbonyl anion that is more nucleophilic than $Mn(CO)_3(PPh_3)_2^-$, a CO^{2+} transfer occurs; a less nucleophilic anion results in SET. Single electron transfer reactions of triphenylphosphine complexes are characterized by formation of hydride products. Transfer of CO^{2+} leads to new cation and anion products.

Keywords: Manganese complexes, carbonyl, phosphine, electron transfer

INTRODUCTION

We have previously reported that reactions between metal carbonyl cations and anions exhibit single electron transfer and CO^{2+} transfer.[1] Similar $1e^-$ and $2e^-$ processes have been reported for other complexes.[2] Rates of SET reactions between metal carbonyl anions and cations are significantly affected by replacing CO with a phosphine ligand.[1] Rates of CO^{2+} transfer are not greatly affected by phosphine substitution.[1] Thus substituted anions and cations have the potential to give very clear evidence for CO^{2+} transfer before SET occurs. In this manuscript we report reactions of $[PPN][Mn(CO)_3(PPh_3)_2]$ and $[Mn(CO)_4(PPh_3)_2][ClO_4]$.

The experimental procedures and syntheses have been previously reported.[1] Products of the reactions are identified by comparison of their infrared absorptions in the carbonyl stretching region to those of authentic samples.

Reactions of $[Mn(CO)_4(PPh_3)_2][ClO_4]$ with metal carbonyl anions, $Mn(CO)_5^-$, and $Mn(CO)_4L^-$ ($L = PPh_3$, PEt_3 and PPh_2Me) result in relatively slow formation of products expected from SET.

$$Mn(CO)_4(PPh_3)_2^+ + Mn(CO)_5^- \rightarrow Mn_2(CO)_{10} + HMn(CO)_4PPh_3 \qquad (1)$$

$$\begin{aligned} Mn(CO)_4(PPh_3)_2^+ + Mn(CO)_4L^- \rightarrow {} & \underset{\text{(major)}}{Mn_2(CO)_8L_2} + \underset{\text{(major)}}{HMn(CO)_4PPh_3} \qquad (2) \\ & + \underset{\text{(minor)}}{Mn_2(CO)_{10}} + \underset{\text{(minor)}}{Mn_2(CO)_9L} \end{aligned}$$

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The hydride is formed readily by hydrogen abstraction reactions of $\cdot Mn(CO)_4PPh_3$. Reactions (*1*) and (*2*) are quite slow, requiring two days for completion. Reaction of $[PPN][Mn(CO)_3(PPh_3)_2]$ with $[Mn(CO)_4(PPh_3)_2^+]$ also produces hydrides.

$$Mn(CO)_3(PPh_3)_2^- + Mn(CO)_4(PPh_3)_2^+ \rightarrow HMn(CO)_4PPh_3 + HMn(CO)_3(PPh_3)_2 \quad (3)$$

This reaction also must occur by SET producing $\cdot Mn(CO)_3(PPh_3)_2$ and $\cdot Mn(CO)_4PPh_3$ which abstract hydrogen to form the hydrides. Reaction of $Mn(CO)_3(PPh_3)_2^-$ with $[CpFe(CO)_3][BF_4]$ and $[Re(CO)_5PPh_3][ClO_4]$ also produce products typical for SET.

$$Mn(CO)_3(PPh_3)_2^- + CpFe(CO)_3^+ \rightarrow Cp_2Fe_2(CO)_4 + HMn(CO)_3(PPh_3)_2 \quad (4)$$

$$Mn(CO)_3(PPh_3)_2^- + Re(CO)_5PPh_3^+ \rightarrow \underset{\text{(major)}}{Re_2(CO)_9PPh_3} + \underset{\text{(major)}}{HMn(CO)_3(PPh_3)_2} \quad (5)$$

$$+ \underset{\text{(minor)}}{Re_2(CO)_{10}} + \underset{\text{(minor)}}{HRe(CO)_4PPh_3}$$

Reaction (*4*) is relatively rapid (a few seconds), but reaction (*5*) requires 10 h, at room temperature.

In contrast to reactions (*1–5*), a number of reactions give clear evidence of CO^{2+} transfer. Reaction of $[PPN][Mn(CO)_3(PPh_3)_2]$ with $[Re(CO)_6][BF_4]$ produces $Mn(CO)_4(PPh_3)_2^+$.

$$Mn(CO)_3(PPh_3)_2^- + Re(CO)_6^+ \rightarrow Mn(CO)_4(PPh_3)_2^+ + Re_2(CO)_{10} \quad (6)$$

In this case the $Re(CO)_5^-$ formed by CO^{2+} transfer to $Mn(CO)_3(PPh_3)_2^-$, rapidly reacts with $Re(CO)_6^+$ to form the dimer, $Re_2(CO)_{10}$.[1] For reaction of $Mn(CO)_3(PPh_3)_2^-$ with $Mn(CO)_6^+$, where subsequent SET is slower, both products of CO^{2+} transfer are observed.

$$Mn(CO)_3(PPh_3)_2^- + Mn(CO)_6^+ \rightarrow Mn(CO)_4(PPh_3)_2^+ + Mn(CO)_5^- \quad (7)$$

In a few days the final products are $Mn_2(CO)_{10}$, $Mn_2(CO)_8(PPh_3)_2$ (minor), $Mn_2(CO)_9PPh_3$ and $HMn(CO)_4PPh_3$. Reaction of $Mn(CO)_5L^+$ with $Mn(CO)_3(PPh_3)_2^-$ produces in seconds the CO^{2+} transfer products, $Mn(CO)_4L^-$ and $Mn(CO)_4(PPh_3)_2^+$ (L = PPh_3, PEt_3 and $PMePh_2$).

$$Mn(CO)_3(PPh_3)_2^- + Mn(CO)_5L^+ \rightarrow Mn(CO)_4(PPh_3)_2^+ + Mn(CO)_4L^- \quad (8)$$

The subsequent SET requires 48 h (reaction *2*).

Reaction of $[PPN][CpFe(CO)_2]$ with $[Mn(CO)_4(PPh_3)_2][ClO_4]$ shows products that do not fit either SET or a CO^{2+} transfer.

$$Mn(CO)_4(PPh_3)_2^+ + CpFe(CO)_2^- \rightarrow Mn(CO)_4PPh_3^- + Cp_2Fe_2(CO)_4 \quad (9)$$

The $Mn(CO)_4PPh_3^-$ slowly converts to $Mn(CO)_5^-$. The presence of the anion $Mn(CO)_4PPh_3^-$ could arise through substitution of a PPh_3 by CO in $Mn(CO)_3(PPh_3)_2^-$ formed by a CO^{2+} transfer or by disproportionation of the odd electron complex, $Mn(CO)_4(PPh_3)_2\cdot$ formed by a SET. ($Cp_2Fe_2(CO)_4$ would be expected from reaction of $CpFe(CO)_2^-$ with $CpFe(CO)_3^+$ formed in a CO^{2+} transfer or from $CpFe(CO)_2\cdot$ dimerization in a SET). Thus reaction (*9*) cannot be assigned a mechanism.

The relatively slow rates of SET reactions of the phosphine substituted manganese cation, $Mn(CO)_4(PPh_3)_2^+$ and anion, $Mn(CO)_3(PPh_3)_2^-$ provide for ease of characterization of the CO^{2+} transfer reactions. For example, $Mn(CO)_3(PPh_3)_2^-$ is cleanly converted to $Mn(CO)_4(PPh_3)_2^+$ in reactions (*6–8*). The disubstituted cation is stable for hours in the reaction mixture. The CO^{2+} transfer reactions reported in this manuscript are observed when the reactant anion is more nucleophilic than the possible product anion,[3] as previously observed.[1] Thus, $Mn(CO)_3(PPh_3)_2^-$ reacts with $Re(CO)_6^+$ and $Mn(CO)_6^+$ by a CO^{2+} transfer, but not with $CpFe(CO)_3^+$. The order for retention of CO^{2+} is $CpFe(CO)_2^- > Re(CO)_4PPh_3^- > Mn(CO)_3(PPh_3)_2^- > Re(CO)_5^- > Mn(CO)_4PPh_3^- > Mn(CO)_5^-$. This order is very similar to that observed for reaction rate with CH_3I.[3] The importance of steric interactions in reactions of metal carbonyl anions with CH_3I has been previously demonstrated.[3] Thermodynamic control of the CO^{2+} transfer can be considered as a competition of two anions; the nucleophilicity of the anions provides a measure of the ability to retain the CO^{2+}. All CO^{2+} transfer reactions occur relatively rapidly (seconds time scale) and do not appear to be significantly affected by steric interactions.

For reactions between a metal carbonyl cation and anion where the reacting anion is less nucleophilic than the product anion in a CO^{2+} transfer, only SET is observed. The products for such reactions (*1–5*), are those expected for odd electron complexes.[1,4] Mixtures of dimers are observed as previously described.[1] In addition, for these disubstituted cations and anions, the substituted radicals abstract hydrogen atoms (presumably from the solvent) to give hydride products.[4] Reaction (*3*) gives only the hydrides $HMn(CO)_4PPh_3$ and $HMn(CO)_3(PPh_3)_2$ as products. Neither the cations ($Mn(CO)_4(PPh_3)_2^+$ and $Mn(CO)_5(PPh_3^+)$) nor the anions ($Mn(CO)_3(PPh_3)_2^-$ and $Mn(CO)_4(PPh_3)^-$) abstract hydrogen from the solvent in the absence of the other. SET provides a reasonable explanation for these reactions. The rates of the SET reactions are significantly affected by steric interactions. Reaction (*4*) and previously reported reactions occur in a few minutes, while reactions where the cation and the anion contain phosphine ligands (reactions *2* and *5*) require hours or even days. The reason for the rate of the SET reaction to be more affected than CO^{2+} transfer by the presence of phosphines on the cation and the anion is not apparent. In organic reactions the S_N2 reaction is more affected by steric interactions than is a SET reaction.

The reactions between disubstituted metal carbonyl cations and anions provide very clear evidence for CO^{2+} transfer when the reactant anion is more nucleophilic than the product anion. The presence of phosphines causes a significant reduction in SET reaction rate, while not significantly affecting the CO^{2+} transfer. This allows the products of CO^{2+} transfer to be readily characterized.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of the Department of Energy, Office of Basic Energy Sciences (DE-FG02-87ER13775.A004) for support of this research.

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