

Kinetics and mechanisms of CO substitution reactions of metal carbonyls

Fred Basolo

Chemistry Department, Northwestern University, Evanston, IL 60201, USA

Abstract - This article mentions briefly some of our early work on the kinetics and mechanisms of CO substitution reactions of metal carbonyls, and it gives an overview of our more recent studies on three different types of systems. These systems are (1) compounds where ring slippage seems to be involved in reaction, (2) heterocyclic metal carbonyls, and (3) 17-electron metal complexes. Experimental details are not given, but these are available in the referenced publications.

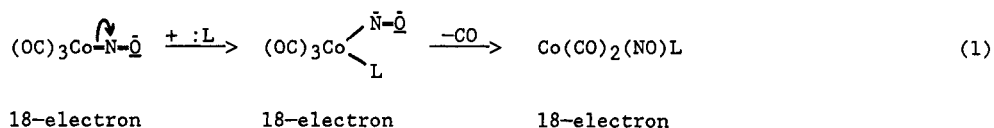
INTRODUCTION

Ligand substitution reactions are essential for the use of transition metal organometallic compounds as homogeneous catalysts. Therefore, it is important that we know what factors affect the rates of reaction and why. Much information, both qualitative and quantitative, is available¹ on the reactivity of organometallic compounds. What is needed are more detailed kinetic studies that give information on the mechanisms of ligand substitution, and on what factors contribute to rates of reaction in these systems. Studies in our laboratory on three different types of systems are described here.

RING SLIPPAGE MECHANISM

About three decades ago we initiated a study of CO exchange using ¹⁴CO, and of CO substitution with P-ligands on binary metal carbonyls. Since very little work² of this type had been done at the time, our observations were often a source of some surprise. For example, Ni(CO)₄ was found³ to exchange CO by a dissociative process, although one might have expected the 4-coordinate complex to readily expand its coordination number to permit a low energy associative pathway for reaction. Today we discuss and understand this behavior in terms of Tolman's⁴ 16-, 18-electron rule. An associative substitution for Ni(CO)₄ would require the formation of an unstable 20-electron transition state or active intermediate, whereas a dissociative process goes through a more stable 16-electron active intermediate.

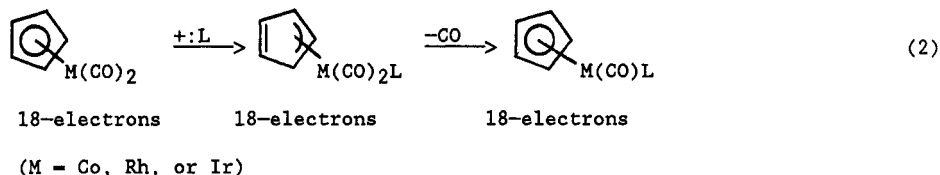
Imagine our surprise at the time to find⁵ that CoNO(CO)₃ and Fe(NO)₂(CO)₂, isoelectronic and isostructural with Ni(CO)₄, both undergo CO substitution by an associative process. The interpretation given this observation, before the 16-, 18-electron rule and before the bent metal nitrosyl, was that a pair of electrons are localized on the nitrosyl group freeing a low energy metal orbital for nucleophilic attack (eq. 1).



Such a process that maintains an 18-electron count throughout is much less available for a compound with only CO ligands because N is more electronegative than C and because the nitrosyl ligand is formally present as NO⁺.

Also surprising, but more readily explained after the nitrosyl ligand experience, was the observation⁶ that the compounds (η⁵-C₅H₅)M(CO)₂ (where M = Co, Rh, or Ir) undergo CO substitution by an associative pathway. Surprising, because these compounds are pseudo-isoelectronic with Fe(CO)₅ which only very slowly reacts thermally by a dissociative process.² More readily interpreted, because after the nitrosyl experience we were prepared to localize a pair of electrons on the cyclopentadienyl ring in order to permit nucleophilic attack of a low energy metal orbital. Some years later it was suggested⁷ that the pair of electrons localized on the cyclopentadienyl ring could be formulated as an η³ allyl-ene system. There is now X-ray evidence⁸ for such a cyclic ligand in the compound

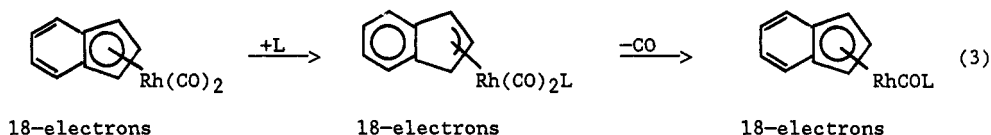
$(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2$. This suggests that an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ associative pathway is involved (eq. 2).



As expected for a mechanism that requires the flow of electron density from the metal into the cyclic ligand, electron withdrawing substituents (NO_2) on the ring enhance rates of CO substitution and electron donating groups (CH_3) on the ring retard rates of substitution.

	$(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$	$(\eta^5\text{-C}_5\text{H}_4\text{NO}_2)\text{Rh}(\text{CO})_2$	$(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{Rh}(\text{CO})_2$
relative rates	1	10^4	10^{-2}

Furthermore a relative rate increase of 10^8 was observed for $(\eta^5\text{-indenyl})\text{Rh}(\text{CO})_2$ over $(\eta^5\text{-cyclopentadienyl})\text{Rh}(\text{CO})_2$, and this has been termed the indenyl ligand effect.⁹ This had been previously observed¹⁰ and explained on the basis of the fused six-ring aromaticity in the transition state tending to drive the associative reaction (eq. 3).

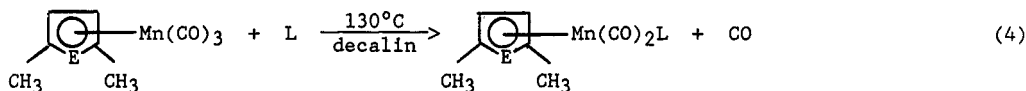


These studies show it is possible to markedly vary (over 10^{10} times) the rates of ligand substitution of organometallic compounds, and if necessary to fine tune these rates for optimum homogeneous catalysis conditions.

HETEROCYCLIC METAL CARBONYLS

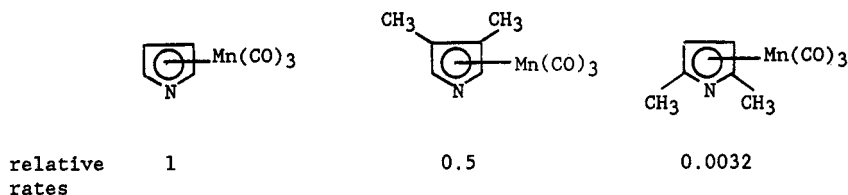
Although thousands of papers have been published on the syntheses and reactions of η^5 -carbocyclic metal carbonyls, much less work has been done with the corresponding η^5 -heterocyclic compounds.¹¹ No work had been reported on the kinetics and mechanisms of CO substitutions of these compounds, so it was decided to mount such an investigation. Compounds, corresponding to known η^5 -cyclopentadienyl metal carbonyls, were prepared and studied that have one heteroatom (N, P, or As) in the 5-membered ring.

The reactions investigated¹² are presented by eq. 4, where E = C, N, P, or As, and L = PR_3 or $\text{P}(\text{OR})_3$.

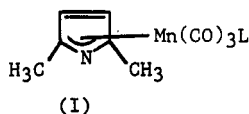


The compounds where E = C, N, P, or As do not react even after 3 days at 130°C . The $(\eta^5\text{-N-heterocycle})\text{Mn}(\text{CO})_3$ does react at these conditions with a second-order rate law, first-order in concentrations of the complex and of the nucleophile. Values of second-order rate constants at 130°C in decalin are $1.2 \times 10^{-6}\text{M}^{-1}\text{s}^{-1}$ for the nucleophile $\text{P}(\text{n-Bu})_3$ and $2.0 \times 10^{-6}\text{M}^{-1}\text{s}^{-1}$ for $\text{P}(\text{OEt})_3$. The tentative interpretation given these observations that only the N-heterocyclic compound reacts is that N is the most electronegative atom used, e.g. N, 3.0; C, 2.5; P, 2.1; As, 2.0. Again the greater electron withdrawing property of the cyclic ligand with the more electronegative N atom seems to enhance the rate of an $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ mechanism.

Another interesting observation¹² was made when the rates of reaction of three $(\eta^5\text{-N-heterocyclic})\text{Mn}(\text{CO})_3$ were compared.

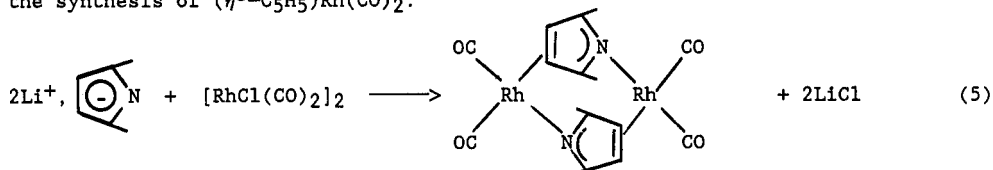


Addition of two methyl substituents which are electron donating to the pyrrolyl ligand are expected to decrease the rate of CO substitution by an associative $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ mechanism. What was not anticipated is that the positions of the methyl groups on the ring would have such a large effect, the 2,5-dimethyl pyrrolyl decreases the rate of substitution 100 times more than does the 3,4-dimethyl pyrrolyl. We suggest this results from a preferred ring slippage towards the formation of an η^3 -2-azaallyl bonding mode of the metal moiety to the pyrrolyl ligand (I)



in the transition state or active intermediate for reaction. This slippage towards nitrogen results in a much more crowded transition state for (I) than for the corresponding 3,4-dimethylpyrrolyl system, and thus a much greater retardation in the rate of CO substitution. Support for ring slippage towards N is provided¹⁴ by the X-ray structure of $(\eta^5$ -3,4-dimethylpyrrolyl) $Mn(CO)_3$ which shows such slippage even in the ground state.

Since only the N-heterocycle compounds $(\eta^5$ -N-heterocycle) $Mn(CO)_3$ react rapidly enough even at 130°C to conduct a kinetic study, it has not been possible to determine if indeed there is a quantitative correlation between the rates of CO substitution and the electronegativity of the hetero atom. This should be possible providing we could prepare the more reactive compounds of the type $(\eta^5$ -heterocycle) $M(CO)_2$, where M = Co, Rh, or Ir. An attempt¹⁵ was made to prepare $(\eta^5$ -2,5-dimethylpyrrolyl) $Rh(CO)_2$ by a reaction (eq. 5) analogous to that used for the synthesis of $(\eta^5$ -C₅H₅) $Rh(CO)_2$.



The desired and expected monomeric $(\eta^5$ -2,5-(CH₃)₂C₄H₂N) $Rh(CO)_2$ was not obtained, so we have as yet been unable to test the concept of reactivity versus the electronegativity of the heteroatom. However, the dimer obtained is the first example of a heterocyclic bridging ligand between two metals utilizing both the σ and the η^2 - π bonding modes of the ligand to form a highly distorted metal-olefin moiety.

17-ELECTRON SYSTEMS

It is well known that for molecular transition metal organometallic compounds 18-electrons is the magic number for maximum stability. A decade ago Brown¹⁶ reported that 17-electron metal carbonyl radicals, such as $Mn(CO)_5$ and $Re(CO)_5$, are substitution labile. These radicals were generated photochemically in solution and studied *in situ*, so we¹⁷ decided to investigate $V(CO)_6$ which is a stable solid 17-electron binary metal carbonyl. Its reactions with phosphines and phosphites (eq. 6)

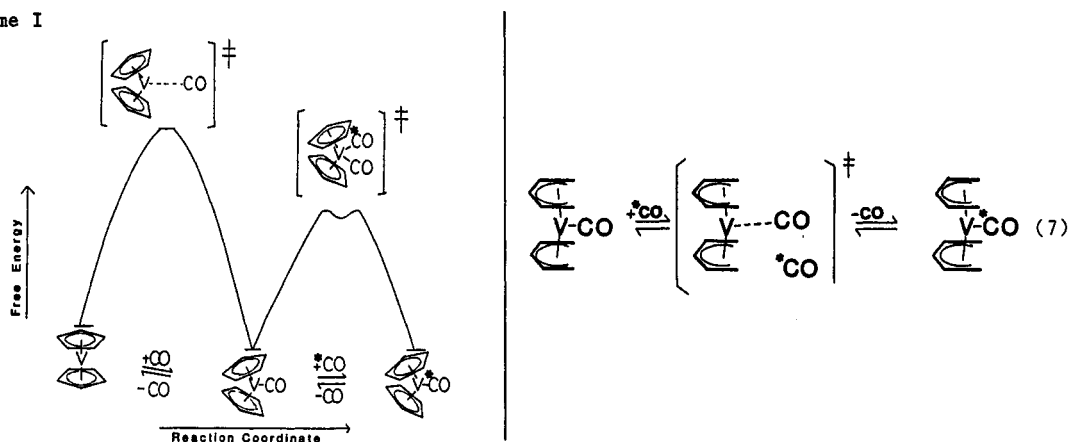


proceed by an associative mechanism. The point of interest here is that it was possible for the first time to quantitatively compare the rates of CO substitution of analogous 17- and 18-electron metal carbonyls.

	$Cr(CO)_6$	$V(CO)_6$
	18-electrons	17-electrons
relative rates	1	10^{10}

This rapid rate of associative ligand substitution of a 17-electron over a corresponding 18-electron metal complex is in accord with the lower energy barrier for the reaction process of 17-electron \rightarrow 19-electron compared to that of 18-electron \rightarrow 20-electron.

Scheme I



This investigation was extended to the reaction of vanadocene, $(\eta^5\text{-C}_5\text{H}_5)\text{V}$, with CO to give the 17-electron adduct $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCO}$ and to its CO exchange kinetics.¹⁸ The rate of CO exchange is fast and it goes by an associative mechanism as proposed by the reaction profile of Scheme I.

Experiments showed that the rate of CO exchange with $(\eta^5\text{-C}_5\text{H}_5)\text{VCO}$ is greater than the rate of addition of CO to vanadocene, which accounts for the higher energy barrier shown in Scheme I. It is believed this is caused by the conformational change required when CO is added to vanadocene, whereas the associative CO exchange takes place without the expenditure of energy required to bend back the cyclopentadienyl rings.

A dramatic change in rate and in mechanism was observed¹⁹ when cyclopentadienyl was replaced by pentadienyl in these systems. The compound $(\eta^5\text{-C}_5\text{H}_7)\text{VCO}$ is substitution inert and substitution takes place by a dissociative pathway. The I_d mechanism proposed for CO exchange is given in eq. 7.

This is the first report of a kinetic study of a 17-electron organometallic compound that is slow to react and that reacts by a dissociative process. The absence of a facile associative substitution pathway in the pentadienyl compounds may be attributed to the more rigid $(\eta^5\text{-C}_5\text{H}_7)_2\text{V}$ moiety, decreased V-CO π -backbonding, or reduced electron spin delocalization, all of which make the metal center less susceptible to nucleophilic attack.

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REFERENCES

1. J. D. Atwood, "Inorganic and Organometallic Reaction Mechanisms", Book/Cole Publishing Co., Monterey, CA, 1985.
2. D. F. Keeley and R. E. Johnson, *Inorg. Nucl. Chem.* **11**, 33 (1959).
3. A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.* **83**, 520 (1961); J. P. Day, R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.* **90**, 6927 (1968).
4. C. A. Tolman, *Chem. Rev.* **77**, 313 (1977).
5. E. M. Thorsteinson and F. Basolo, *J. Am. Chem. Soc.* **88**, 3929 (1966); D. E. Morris and F. Basolo, *ibid.* **90**, 2531 (1968).
6. H. G. Schuster-Woldan and F. Basolo, *J. Am. Chem. Soc.* **88**, 1657 (1966).
7. R. Cramer and L. P. Seiwel, *J. Organometal. Chem.* **92**, 245 (1975).
8. G. Huttner, H. H. Brintzinger, L. G. Bell, P. Friedlich, V. Bejenki and D. Neugebauer, *J. Organomet. Chem.* **145**, 329 (1978).
9. L. N. Ji, M. E. Rerek and F. Basolo, *Organometallics* **3**, 740 (1984).
10. A. J. Hart-Davis and R. J. Mawby, *J. Chem. Soc. A* 2403 (1969); D. J. Jones and R. J. Mawby, *Inorg. Chim. Acta* **6**, 157 (1972).
11. M. Novi, G. Guiseppe and C. Dell'Erba, *J. Het. Chem.* **12**, 1055 (1975); D. L. Kershner and F. Basolo, *Coord. Chem. Rev.*, in press.
12. D. L. Kershner and F. Basolo, *J. Am. Chem. Soc.*, in press.
13. R. S. Angelici and W. Lowen, *Inorg. Chem.* **6**, 682 (1967).
14. D. L. Kershner, A. L. Rheingold and F. Basolo, *Organometallics* **6**, 196 (1987).
15. K. Yünlü, A. L. Rheingold and F. Basolo, *J. Organomet. Chem.*, in press.
16. D. R. Kidd and T. L. Brown, *J. Am. Chem. Soc.* **100**, 4095 (1978); T. L. Brown, *Ann. N.Y. Acad. Sci.* **333**, 80 (1980).
17. Q. Z. Shi, T. G. Richmond, W. C. Trogler and F. Basolo, *J. Am. Chem. Soc.* **106**, 71 (1984).
18. R. M. Kowaleski, F. Basolo, W. C. Trogler, R. W. Gebridge, T. D. Newbound and R. D. Ernst, *J. Am. Chem. Soc.*, in press.
19. R. M. Kowaleski, F. Basolo, W. C. Trogler and R. D. Ernst, *J. Am. Chem. Soc.* **108**, 6046 (1986).