Journal of Organometallic Chemistry, 172 (1979) C7—C12

PRELIMINARY COMMUNICATION

SYNTHESIS OF ALLYL COMPLEXES OF IRON, MANGANESE AND MOLYBDENUM BY PHASE TRANSFER CATALYSIS

Dorothy H. Gibson, Wen-Liang Hsu and Da-Sheng Lin

Department of Chemistry, University of Louisville, Louisville, Kentucky 40208

(Received March 2nd, 1979)

SUMMARY

Synthetic methods are described for the convenient and efficient preparation of σ- and π-allyl complexes of iron, manganese and molybdenum from metal carbonyl halides and allyl halides in phase transfer catalyzed reactions.

Allyl transition metal complexes have much utility in organometallic chemistry as catalysts and reaction intermediates.[1] Synthetic methods for the preparation of both the σ- and π-complexes have been available for two decades, but most of the methods require initial generation of a metal carbonyl anion in a time-consuming step.[2] In many cases, the π-complex is not obtained directly and must be prepared after tedious isolation of a usually air-sensitive σ-complex.[3] Several years ago, Abel and Moorhouse[4] reported an alternate route to the π-complexes utilizing metal carbonyl halides together with allyl tin derivatives. These reactions offer some advantages for the preparation of the π-complexes since the yields are moderate to good and the reaction times are usually not long. However, it is necessary to prepare the intermediate allyl tin compounds (which do not have long shelf lives) and to separate the final product from a tin halide at the end of the sequence.

Much more recently, Alper[5] and his coworkers have reported that allyl cobalt derivatives could be obtained from $Co_2(CO)_8$ and allyl halides in phase transfer catalyzed (PTC) reactions. In trying to adapt this technique ourselves to other metal carbonyls as well as to some systems already bearing an organic ligand, we found that the method did not work well.

We wish to report a new synthetic route to π-allyl complexes which can also be adapted, with some systems, to provide the σ-complex instead. The reactions utilize easily available (and stable) metal carbonyl halides together with allyl halides in benzene or dichloromethane as the organic phase and benzyltriethylammonium chloride as the phase transfer catalyst in aqueous NaOH. The results of our work are summarized in Table 1.

Table 1. Phase transfer catalyzed reactions of metal carbonyl halides with allyl halides.

Reactants	Solvent/Temperature/Time/Method[a]	Product	% Yield
$Mn(CO)_5Br$[6] + C_3H_5Br	CH_2Cl_2/reflux/5 hrs./A	π-$C_3H_5Mn(CO)_4$[3]	80
Same	C_6H_6/60°/4-5 hrs./A	π-$C_3H_5Mn(CO)_4$	60
$Mn_2(CO)_8Cl_2$[7] + C_3H_5Br	C_6H_6/24°/1 hr./A	π-$C_3H_5Mn(CO)_4$	40
Same	C_6H_6/24°/1 hr./A[b]	π-$C_3H_5Mn(CO)_4$	39
$Mn(CO)_5Br$ + 2-CH_3-C_3H_4Cl	CH_2Cl_2/reflux/12 hrs./A	2-CH_3-π-$C_3H_4Mn(CO)_4$[3]	48
$Mn(CO)_4P\phi_3Br$[8] + C_3H_5Br	CH_2Cl_2/reflux/1 hr./A	π-$C_3H_5Mn(CO)_3P\phi_3$[c]	90
π-$C_3H_5Fe(CO)_3Br$[9] + C_3H_5Br	CH_2Cl_2/24°/1 hr./A	bis-π-$C_3H_5Fe(CO)_2$[10]	76
$CpMo(CO)_3Cl$[11] + C_3H_5Br	C_6H_6/45°/8 hrs./B	π-$C_3H_5(Cp)Mo(CO)_2$[12]	95
$CpMo(CO)_3Cl$ + C_3H_5Br	CH_2Cl_2/24°/5 hrs./A	σ-$C_3H_5(Cp)Mo(CO)_3$[12].	75
$CpFe(CO)_2Cl$[13] + C_3H_5Br	C_6H_6/24°/4 hrs./B	π-$C_3H_5(Cp)Fe(CO)$[2]	60[d]
$CpFe(CO)_2Br$[14] + C_3H_5Br	C_6H_6/24°/4 hrs./B	π-$C_3H_5(Cp)Fe(CO)$	60
$CpFe(CO)_2Br$ + C_3H_5Br	CH_2Cl_2/24°/2 hrs./A	σ-$C_3H_5(Cp)Fe(CO)_2$[2] + $[CpFe(CO)_2]_2$	36,30

[a] See Experimental for a complete description of methods A and B. [b] Carbon monoxide was bubbled into the mixture during the first five minutes of the reaction. [c] m.p. 120-125° dec.; IR $\nu_{C\equiv O}$(hexane) 2002, 1940, 1912 cm^{-1}; PMR(C_6D_6) 7.19 δ (multiplet, 15 H), 3.93 δ (multiplet, 1H), 2.24 δ (doublet, 2H) and 1.86 δ (pair of doublets, 2H).
[d] The crude product contains a small amount of σ-complex.

These reactions provide the allyl complexes in high yields after short times and easy work-up procedures (see experimental methods). In most cases they are far superior to currently available methods as the following two examples will demonstrate: the present method for π-$C_3H_5CpFe(CO)$ requires[2] about 10 hours and proceeds in overall 27% yield whereas our method yields the π-complex in 60% yield from $CpFe(CO)_2Br$ after only 4 hours; the present methods[4,15] for π-$C_3H_5CpMo(CO)_2$ require 40-120 hours to give yields of 60% whereas our method provides this compound in 95% yield from $CpMo(CO)_3Cl$ after only 8 hours. Furthermore the procedures avoid the use of dangerous and moisture-sensitive reagents such as sodium amalgam[2a] or potassium hydride.[2b,d]

The reactions of transition metal carbonyls with hydroxide ion are, in general, not very well understood at present. One proposed intermediate results from direct addition of hydroxide ion to a carbonyl ligand; subsequently this intermediate may decarboxylate or serve to labilize the metal carbonyl toward substitution by a second nucleophile:[16]

$$\begin{tikzcd}
M(CO)_x + {}^-OH \arrow[r] & {[M(CO)_{x-1}COOH]^-} \arrow[r, "-CO_2"] \arrow[dl, "\begin{array}{l}+L\\-CO\end{array}"'] & HM(CO)^-_{x-1} \\
{[LM(CO)_{x-2}COOH]^-} \arrow[r, "-OH^-"] & LM(CO)_{x-1} &
\end{tikzcd}$$

Alternatively, Alper[5] has provided strong evidence that $Co(CO)_4^-$ is the major product resulting from hydroxide ion attack on $Co_2(CO)_8$ in PTC reactions. In synthesizing π-allyl cobalt complexes in this way, Alper proposed that an unstable σ-complex might be intermediate.

The σ-allyl Fe and Mo complexes in Table I are known[2,12] to require photolysis to induce decarbonylation, thus it is perhaps not surprising that the PTC reaction conditions can be adjusted to provide these instead of the π-complexes. However, σ-$C_3H_5Mn(CO)_5$ is also known[3] to require forcing conditions (heating for several hours at 80°) to cause its conversion to the π-complex, yet it is not seen as a reaction product. In thinking that OH^- might be functioning as a labilizing agent for σ-π conversion, we have treated both σ-$C_3H_5Mn(CO)_5$ and σ-$C_3H_5CpMo(CO)_3$ with the PTC reagent and NaOH. In neither case does σ-π conversion take place.

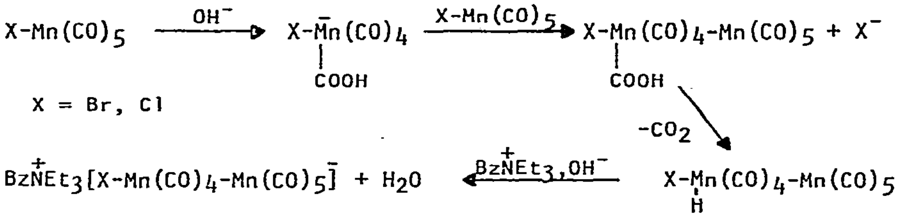
Reactions of the manganese carbonyl halides conducted under PTC conditions without an allyl halide provide products which appear as intermediates in the syntheses of the allyl complexes. These compounds are completely formed in the first 15 minutes of the reactions and it is these which are converted by subsequent reactions to the final π-complexes by processes which require the PTC reagent as well as an allyl halide. Intermediates derived from $Mn(CO)_5Br$* and $Mn(CO)_5Cl$** have been isolated and characterized as binuclear anionic complexes of the type formed from photolysis of $Mn_2(CO)_{10}$ in the

---

*$Bz\overset{+}{N}Et_3[Br\text{-}Mn(CO)_4\text{-}Mn(CO)_5]^-$: m.p. 93-94°; IR $\nu_{C\equiv O}(CH_2Cl_2)$ 2080(W), 2010(S), 1980(vs), 1970(vs), 1945(m) and 1903(m); isolated in 84% yield.

**$Bz\overset{+}{N}Et_3[Cl\text{-}Mn(CO)_4\text{-}Mn(CO)_5]^-$: m.p. 85-87°; IR $\nu_{C\equiv O}(CH_2Cl_2)$ 2080(w), 2010(s), 1980(vs), 1970(vs), 1950(m) and 1905(m); isolated in 82% yield from PTC reaction of $Mn(CO)_5Cl$ and identical with a sample prepared from $BzNEt_3Cl$ and $Mn_2(CO)_{10}$.[17]

presence of quaternary ammonium halides.[17] In the PTC reactions, we believe these may be formed as follows:



A

The route by which compounds of structure A are converted to the final π-allyl products is presently under study. It is hoped that these reactions may contribute some additional insight into the general questions surrounding nucleophilic additions to metal carbonyls.[18]

The metal carbonyl systems used thus far contain either chlorine or bromine with one exception: $CpFe(CO)_2I$. The iodide was found to be much less reactive than the chloride and bromide. This order of reactivity parallels the behavior of metal carbonyl halides in some other reactions which involve loss of the halogen,[11] but phase transfer phenomena may be responsible instead.[19] Only when the mechanism of these reactions is more clearly understood will we be able to answer this question.

Experimental:

All reactions were carried out under dry nitrogen. Benzene, dichloromethane and allyl bromide were distilled before use. The following compounds were prepared as described previously: $Mn(CO)_5Br$[6], $CpMo(CO)_3Cl$[11], $CpFe(CO)_2Br$[14], $CpFe(CO)_2Cl$[13], $Mn(CO)_4(P\O_3)Br$[8]; $Mn_2(CO)_{10}$ was purchased from Strem Chemical Co. and used without further purification. The following compounds were prepared by slightly modified literature procedures: a) $Mn_2(CO)_8Cl_2$[7]: $Mn(CO)_5Cl$[20] was heated in a slurry with heptane at 45° for 2 hours with nitrogen slowly bubbling through the solution (product yield: 90%); b) $(\pi\text{-}C_3H_5)Fe(CO)_3Br$[9]: a slurry of $Fe_2(CO)_9$[21] and allyl bromide (1:1) in benzene was heated at 40° for 1 1/2 hours, filtered and the solvent removed by evaporation (product yield after crystallization from hexane/CH_2Cl_2: 70%). Benzyltriethylammonium chloride was obtained from Aldrich Chemical Co. and used directly.

Method A

Benzyltriethylammonium chloride, 1.5 m moles, was dissolved in 45 ml of 5N NaOH and added to a stirred solution containing 15 m moles of allyl bromide and 3 m moles of the metal carbonyl halide in benzene or dichloromethane (see Table I for the solvent used with a particular compound). After the reaction was over, the organic layer was separated, washed with water and then dried over $MgSO_4$. After solvent evaporation, the crude product was purified as described previously. The new compound, π-$C_3H_5Mn(CO)_4(P\phi_3)$, was purified by chromatography on silica gel.

Method B

A solution containing 1 m mole of the metal carbonyl halide in 15 ml of benzene was added slowly to a mechanically stirred mixture containing 5 m moles of benzyltriethylammonium chloride, 20 ml of 5N NaOH and 10 m moles of allyl bromide in 15 ml of benzene. After completion of the reaction, the benzene layer was separated, washed and then dried over $MgSO_4$. After solvent evaporation, the crude product was purified by vacuum sublimation.

Acknowledgment

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and to the Arts and Sciences Research Committee for a grant.

References

1. G. P. Chiusoli and L. Cassar in *Organic Syntheses via Metal Carbonyls*, Vol. II, p. 297, I. Wender and P. Pino, eds., Wiley-Interscience, New York, 1977.

2. a) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963); b) J. A. Gladysz, G. M. Williams, W. Tam and D. L. Johnson, *J. Organometal. Chem.*, 140, C1 (1977); c) K. Inkrott, R. Goetze and S. G. Shore, *ibid.*, **154**, 337 (1978) and d) J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker and J. C. Selover, *Inorg. Chem.*, **18**, 553 (1979).

3. See, for example, W. R. McClellan, H. H. Hoehn, H. M. Cripps, E. L. Muetterties and B. W. Howk, *J. Amer. Chem. Soc.*, **83**, 1601 (1961).

4. E. W. Abel and S. Moorhouse, *J. Chem. Soc. Dalton*, 1706 (1973).

5. H. Alper, H. des Abbayes and D. des Roches, *J. Organometal. Chem.*, **121**, C31 (1976).

6. E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

7. F. Zingales and V. Santorelli, *Inorg. Chem.*, **6**, 1243 (1967).

8. A. M. Bond, R. Colton and M. E. McDonald, *ibid.*, **17**, 2842 (1978).

9. G. F. Emerson, Ph.D. Thesis, University of Texas, 1964.

10. A. M. Nesmayanov, Yu. A. Ustynyuk, I. I. Kritskaya and G. A. Shchembelov, *J. Organometal. Chem.*, **14** 395 (1968).

11. C. White and R. J. Mawby, *Inorg. Chim. Acta*, **4**, 261 (1970).

12. M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

13. T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1956).

14. B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 3030 (1956).

15. J. W. Faller, C.-C. Chen, M. J. Mattina and A. Jakubowski, *J. Organometal. Chem.*, **52**, 361 (1973).

16. See D. J. Darensbourg and J. A. Froelich, *J. Amer. Chem. Soc.*, **100**, 338 (1978) and references cited therein.

17. J. L. Cihonski and R. A. Levenson, *Inorg. Chim. Acta*, **18**, 215 (1976).

18. T. L. Brown and P. A. Bellus, *Inorg. Chem.*, **17**, 3726 (1978).

19. D. Landini, A. Maia, and I. Montanari, *J. Amer. Chem. Soc.*, **100** 2796 (1978).

20. M. S. Wrighton and D. S. Ginley, *ibid.*, **97**, 2065 (1975).

21. The $Fe_2(CO)_9$ was made by a modification of the procedure of R. B. King: Organometallic Synthesis, Vol. 1, Transition Metal Compounds, Academic Press, New York, 1965, p. 93, in which acetic anhydride was used as the reaction solvent.