

TRANSITION METAL PROMOTED REACTIONS

XI *. TRIMETHYLAMINE-*N*-OXIDE PROMOTED σ - TO π -ALLYL REARRANGEMENT. A CONVENIENT SYNTHESIS OF $\text{CpMo}(\text{CO})_2(\pi\text{-ALLYL})$

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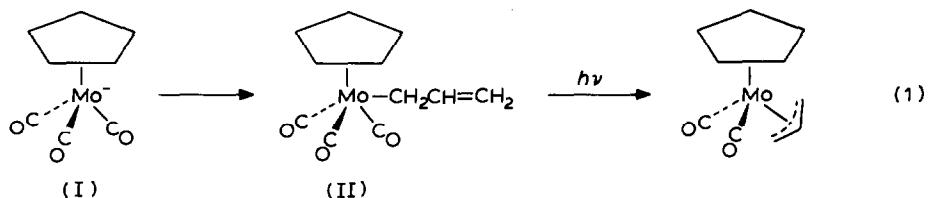
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Summary

Trimethylamine-*N*-oxide was found to be an active reagent for the promotion of σ - to π -allyl rearrangement. Several $\text{CpMo}(\text{CO})_2(\pi\text{-allyl})$ complexes were conveniently synthesized in good yields.

The rearrangement of a σ -allyl complex to a π -allyl complex is important in organometallic reactions [2]. In general, if the loss of a ligand generates a coordinatively unsaturated metal and if a σ - to π -rearrangement satisfies the coordination requirement by the donation of one or more than one pair of electrons, such a rearrangement will occur. There are various methods of promoting such reactions. As an illustration, σ -allyl complexes of cyclopentadienyltricarbonyl-molybdenum [3] and -tungsten [4] yielded the corresponding π -complexes upon irradiation (eq. 1).



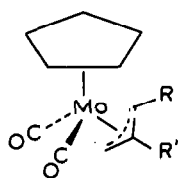
However, the yields were only moderate and the thermal reaction gave even poorer yields [3]. Although the π -complexes can be synthesized by other routes [5], we felt that the transformation from the σ - to the π -allyl complex shown in eq. 1 could be achieved by using reagents other than light or heat. Various reagents can induce ligand displacement reactions of metal carbonyls [6]; trimethylamine-*N*-oxide has

* For part X see Ref. 1.

been found to be extremely useful in organometallic reactions [7]. Hence, the latter compound could be used for the intramolecular rearrangement of allyl complexes. The σ -complex II can be readily synthesized by an S_N2 reaction [3]. We felt that the π -allyl complex could be obtained in a "one-pot" reaction from the anion I without isolation of II. Thus, σ -allylcyclopentadienyltricarbonylmolybdenum generated in situ according to the literature procedure [3] was treated with trimethylamine-*N*-oxide to afford the desired π -allyl complex in 75% yield. In a similar manner, π -crotyl, π -methallyl and η^3 -benzyl complexes were synthesized in good to excellent yields.

The general criterion for the reaction of an amine oxide with a metal carbonyl is $K > 16$ [7,8]. Brown and co-workers found that $\text{CpMo}(\text{CO})_3\text{CH}_3$ ($K = 15.8$) does not undergo an intermolecular CO ligand displacement reaction in the presence of trimethylamine-*N*-oxide [9]. It is interesting to note that the adsorptions in the carbonyl region for $\text{CpMo}(\text{CO})_3(\sigma\text{-CH}_2\text{CH}=\text{CH}_2)$ (2021, 1949 cm^{-1}) and for $\text{CpMo}(\text{CO})_3\text{CH}_3$ (2018, 1950, 1946 cm^{-1}) [9,10] are very similar. The mechanism for the amine oxide-catalyzed decarbonylation reaction is generally believed to occur by nucleophilic attack at the carbonyl carbon by the oxygen end of the amine oxide [7,11]. Therefore, such a discrepancy is somewhat striking. Presumably, the olefinic moiety in the σ -allyl complex may play a role in this reaction; the intermolecular displacement of a CO ligand by an olefin moiety is well documented [7,17]. However, a recent report on a ruthenium complex also showed that such a barrier ($K > 16$) can be overcome by choosing appropriate conditions [12].

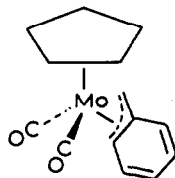
In summary, we have depicted the first example of trimethylamine-*N*-oxide promoted σ - to π -allyl rearrangement. The reaction can serve as a convenient synthesis of $\text{CpMo}(\text{CO})_2(\pi\text{-allyl})$ complexes.



(III, R = R' = H ;

IV, R = Me, R' = H ;

V, R = H, R' = Me)



(VI)

Experimental

Materials

All reactions were carried out under nitrogen gas using standard inert atmosphere techniques. THF was distilled from sodium/potassium and benzophenone. All other solvents were dried and distilled under nitrogen atmosphere. Cyclopentadienyltricarbonylmolybdenum dimer [13] was prepared according to a literature procedure. Commercially available allyl halides were distilled before use. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. NMR spectra were taken on JEOL C-60 HL and Bruker WM250 spectrometers. Mass spectra were measured on a VG 7070F mass spectrometer.

$\text{CpMo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_5)$ (III)

$(\text{CpMo}(\text{CO})_3)_2$ (0.46 g, 0.95 mmol) in THF (ca. 80 ml) was mixed with sodium

amalgam prepared from sodium (0.066 g 2.6 mg-atom) and mercury (20 g). After the solution turned yellow, excess mercury was separated. Allyl bromide (0.87 g, 7 mmol) in THF (10 ml) was then added to the above solution. The mixture was stirred for 4 h at room temperature. Trimethylamine-*N*-oxide (0.4 g, 5 mmol) was then added. The slurry was stirred for another 4 h and then filtered. The filtrate was evaporated and redissolved in petroleum ether and filtered through alumina again. The filtrate was evaporated to give III (0.37 g, 75%); IR $\nu(\text{CO})$ (in C_6H_{12}) 1974, 1966, 1951, 1890 cm^{-1} [3]; $^1\text{H NMR } \delta(\text{CDCl}_3)$: 5.15(5H, s), 4.00(1H, m), 2.90(2H, m), 1.0(2H, m); $^{13}\text{C NMR } \delta(\text{CDCl}_3)$: 38.8, 66.2, 90.2, 236.2.

$\text{CpMo}(\text{CO})_2(\eta^3\text{-CH}_2\text{-CH=CHCH}_3)$ (IV)

A similar reaction of $[\text{CpMo}(\text{CO})_3]_2$ (2.1 g, 4.2 mmol), crotyl chloride (1.52 g, 7 mmol) and then trimethylamine-*N*-oxide (1.3 g, 17 mmol) gave IV (1.86 g, 82%); IR $\nu(\text{CO})$ (in C_6H_{12}) 1968, 1960, 1899, 1885 cm^{-1} ; $^1\text{H NMR } \textit{exo}$ isomer $\delta(\text{CDCl}_3)$: 5.15(5H, s), 3.5–4.00(1H, m), 2.46(1H, dd) 1.70(4H, m), 1.26(1H, m); *endo* isomer, 5.15(5H, s), 3.8–4.0 (2H, m), 2.70(1H, dd), 1.25(1H, m), 0.87(3H, d) [14].

$\text{CpMo}(\text{CO})_2(\eta^3\text{-CH}_2\text{-C}(\text{CH}_3)\text{-CH}_2)$ (V)

$[\text{CpMo}(\text{CO})_3]_2$ (0.5 g, 1 mmol), methylal chloride (1 g, 10 mmol) and then trimethylamine-*N*-oxide (0.44 g, 6 mmol) were treated as described above to afford V (0.38 g, 68%); IR $\nu(\text{CO})$ (in C_6H_{12}) 1969, 1900 cm^{-1} [15].

$\text{CpMo}(\text{CO})_2(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$ (VI)

$[\text{CpMo}(\text{CO})_3]_2$ (1.83 g, 3.73 mmol), benzyl chloride (0.84 g, 6.6 mmol) and trimethylamine-*N*-oxide (1.1 g, 14.7 mmol) were transformed according to the procedure described above into the desired product VI (1.17 g, 51%), which exhibited identical spectroscopic properties to the literature data [16].

References

- 1 T.-Y. Luh, K.S. Lee and S.W. Tam, *J. Organomet. Chem.*, 248 (1983) 221.
- 2 For a review see, M. Tsutsui and A. Courtrey, *Adv. Organomet. Chem.*, 16 (1977) 241.
- 3 M. Cousins and M.L.H. Green, *J. Chem. Soc.*, (1963) 889.
- 4 M.L.H. Green and A.N. Stear, *J. Organomet. Chem.*, 1 (1964) 230.
- 5 E.W. Abel and S. Moorhouse, *J. Chem. Soc., Dalton Trans.*, (1973) 1706; D.H. Gibson, W.L. Hsu and D.S. Lin, *J. Organomet. Chem.*, 172 (1979) C7; R.G. Hayter, *J. Organomet. Chem.*, 13 (1968) P1.
- 6 M.O. Albers and N.J. Coville, *Coord. Chem. Rev.*, 53 (1984) 227.
- 7 T.-Y. Luh, *Coord. Chem. Rev.*, 60 (1984) 255.
- 8 U. Koelle, *J. Organomet. Chem.*, 133 (1977) 53.
- 9 D.J. Blumer, K.W. Barnett and T.L. Brown, *J. Organomet. Chem.*, 173 (1979) 71.
- 10 R.B. King and L.W. Houk, *Can. J. Chem.*, 47 (1969) 2959.
- 11 J. Elzinga and H. Hogeveen, *J. Chem. Soc., Chem. Commun.*, (1977) 705.
- 12 D.S.C. Black, G.B. Deacon and N.C. Thomas, *Inorg. Chim. Acta*, 65 (1982) L75.
- 13 R.B. King, *Organometallic Synthesis*, Vol. 1, Academic Press, New York, 1965, p. 109.
- 14 J.Y. Mérou, C. Charrier, J. Benaim, J.L. Roustan and D. Commereuc, *J. Organomet. Chem.*, 39 (1972) 321.
- 15 J.W. Faller and M.J. Inorvia, *Inorg. Chem.*, 7 (1968) 840.
- 16 R.B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, 88 (1966) 709.
- 17 Y. Shvo and E. Hazum, *J. Chem. Soc., Chem. Commun.*, (1975) 829.